



SEMI-MICRO QUALITATIVE INORGANIC ANALYSIS

Principles : Techniques : Methodologies : Applications



G. N. MUKHERJEE

Sir Rashbehary Ghose Professor &

Chairman, Under Graduate Board of Studies in Chemistry

UNIVERSITY OF CALCUTTA

150 Years of Excellence



Semi-Micro Qualitative Inorganic Analysis
Principles : Techniques : Methodologies : Applications

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PREFACE

The idea of writing a book on *Semi-Micro Qualitative Inorganic Analysis* primarily originated from the deliberations of the seminar on "Chemistry Honours (1+1+1) Curricula" organized by the Under Graduate Board of Studies in Chemistry in collaboration with the Department of Chemistry, University of Calcutta on March 23, 2006, for restructuring the syllabus of Chemistry Honours course, to meet the requirements of the three part B. Sc. (Honours) Degree Examination, subsequently introduced in the University from the 2006-2007 academic session. Chemistry Honours practical course under the (1+1+1) system has now been divided into three parts:

Part-I (First year) : (Paper-II : Group-B, 50 Marks) :

Elementary Physical Chemistry Experiments and Qualitative Organic Analysis.

Part-II (Second year) : (Paper-IV : Group-B, 50 Marks) :

Qualitative Inorganic Analysis.

Part-III (Third year) : (Papers-VII + VIII) Combined (200 Marks) :

Group-A : Advanced Physical Chemistry Experiments, Group-B : Advanced

Inorganic Chemistry Experiments (Quantitative Inorganic Analysis), Group-C :

Advanced Organic Chemistry Experiments (Typical Organic Reactions, Quantitative Analysis of Single Organic Compounds and Chromatographic Separations).

The book entitled, *University Hand Book of Under Graduate Chemistry Experiments* (compiled by Prof. S.B. Chakraborty of R.K. Mission Vivekananda Centenary College, Dr. D.K. Hait and Dr. S.K. Mukherjee of St. Paul's Cathedral Mission College, Dr. S.N. Bhattacharya of the Department Chemistry, C.U., Dr. Rana Sen of Scottish Church College, and Dr. N.C. Ganguli of the Department of Chemistry of Kalyani University and edited by the present author), published by the University in 2003, covers the entire practical course of Chemistry Honours Part-III Examination (Papers VII+VIII), the Elementary Physical Chemistry Experiments (Part of Paper-II Group-B) of B.Sc. Part-I Chemistry Honours Practical Examination and also the practical course on Application Oriented Chemistry of the Chemistry (Elective) Paper-IV (Part-B) of B.Sc. Part-III (General) Degree Examination under the (1+1+1) examination system.

The present book covers the entire practical course (Paper-IV : Group-B) of B.Sc. Part-II Chemistry Honours Practical Examination as well as the Qualitative Inorganic Analysis (Part of Practical Paper-III) of the B.Sc. Part-II General Degree Course Examination in Chemistry (Elective) under the (1+1+1) examination system. The book has been divided into 10 chapters. The introductory chapter (Chapter-1) emphasizes the high degree of precision and sensitivity that could be achieved in semi-micro tests and their advantages over the commonly practiced macro analysis with regard to cost effectiveness, health hazards and environmental considerations. Theoretical basis of the chemical reactions involved in qualitative inorganic analysis have been discussed along with examples and exercises in Chapter-2, which also covers a major part of the Unit-3, entitled, "*Aspects of Inorganic Reactions*" of Group-A of the Chemistry Honours Theoretical Paper-II of B.Sc. Part-I Examination and also a part of Unit-3 of Chemistry (Elective) Paper-II of B.Sc. Part-II (General) Examination under the (1+1+1) system. Techniques and methodologies, apparatus and reagents required for qualitative inorganic

analysis with illustrative diagrams have been detailed in Chapter-3. Chapters-4 and 5 deal with the reactions and semi-micro tests of the individual cation and anion radicals respectively, included in the Chemistry Honours Practical (Paper-IV : Group-B) and also Chemistry (Elective) Practical Paper-III, theoretical Paper-I (Unit-4, Part-c) and Paper-II (Unit-4, Part-c). These should also cover the equivalent curricula of most other Universities in India. Methods of detection of cation and anion radicals and identification of insoluble materials in known inorganic samples by preliminary examinations and by systematic and semi-micro tests have been discussed in Chapters-6 and 7 respectively. Semi-micro tests for the radicals derived from some rare elements have been discussed in Chapter-8 to meet the requirements of PG Chemistry Curricula, recommended by the U.G.C. (2001) and duly adopted by Calcutta University and most other Universities in India. Chapter-9 deals with the qualitative analysis of unknown inorganic samples by semi-micro tests, providing an outline of the procedure for recording the experiments and observations, formulating the inferences and assigning the probable compositions. In the concluding chapter (Chapter-10), applications of spot reactions for detection of trace quantities of some selected elements in real samples have been briefly discussed. Some relevant physical constants, lists of common and special reagents required for qualitative inorganic analysis including the methods of their preparation are given in the Appendix. A list of reference books is added at the end.

The book is expected to fulfil the long standing need of a comprehensive text on semi-micro qualitative inorganic analysis for the B.Sc. Chemistry (Honours and General Standards) of our University and also for Chemistry Major or equivalent standards of other Universities in India. It would also serve as a hand-book of qualitative inorganic analysis for the PG level Chemistry Curricula of most Indian Universities. Suggestions for further improvement of this book are most welcome. The author would highly appreciate the users in pointing out printing errors, omissions, repetitions, if any, so that these could be taken care of in the future editions.

I am grateful to the authority of the University of Calcutta for publishing this book from the University Press. It had been my good fortune, during my PG studies at the University College of Science, to have come in contact with exceptional and inspiring teachers like, Late Prof. N.N. Ghosh, Late Prof. K.L. Roy, Prof. H.K. Saha and Prof. P. Bandyopadhyay, who through their teaching and laboratory sessions, had planted the seeds that grew into the present volume. I had been immensely benefited by numerous questions put forward to me by my students who did never allow me to relax with the false feeling of "knowing every thing". My sincere thanks are due to my colleagues, Prof. S.K. Bose, Prof. S.S. Mandal and Prof. S.K. Kar for learned discussions and to Dr. T.K. Roychaudhuri (Charu Chandra College), Dr. B.N. Mallick (Bangabasi College), Dr. Sadananda Bhattacharya (Scottish Church College) and Dr. D.D. Mukherjee (Mahadevananda Mahavidyalay) for encouragement. I am grateful to Mr. Manas Sutradhar and Miss. Tannistha Roy Barman, Research Scholars, for computer designing of some of the diagrams and searching the internet and to Mrs. Ranjana Dutta, Technical Assistant, for help.

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CHAPTER - 1

Introduction

1.1 Qualitative Analyses

The term "*Qualitative Analysis*" refers to those analytical methods whose goal is to "*detect*" individual elements, ions, (called *radicals*) present in a substance. On the other hand, the analytical methods whose prime objective is to determine (or estimate) the quantities of individual elements or components of a substance are called "*Quantitative Analysis*". Both these analyses maybe carried out by a variety of methods ranging from chemical, through physicochemical to physical. The chemical methods of qualitative analysis involve some chemical transformation of the element or ion of interest into some new compound or a material having specific properties such as colour, solubility or insolubility, physical state etc., which are distinctly different from those of the substance (*sample*) under experiment (*test*) and also different from those of the chemicals (*reagents*) added if any.

Qualitative analyses are distinguished as *macro*, *semi-micro* and *micro* analyses on the basis of techniques and methodology of approach and also on the basis of amounts of the substances detectable or amount or volume of the sample used for analysis.

Table-1.1 : Types of Qualitative Analyses

<i>Characteristics</i>	<i>Macro</i>	<i>Semi-micro</i>	<i>Micro</i>
Amount of substance Weight Volume	0.5 – 1 g 20 – 50 ml	20 – 50 mg 0.1 – 1 ml	1 – 10 mg 0.1 ml
Identification limit*	–	10 – 200 γ	10 γ
Apparatus used	Beakers Flasks Test tubes	Filter paper strips Spot plates Micro crucibles Microtubes	Micro slides Microscopes
Separation techniques	Filtration with filter paper	Centrifugation Capillary separation	Crystals examined under microscope
Procedure/ Reactions	Precipitation Colouration Gas evolution	Spot tests	Micro crystallography Drop methods Spot tests

Gama (γ) = 10^{-6} g = microgram μg .

* (cf p. 3)

Spot test techniques are termed as *semi-micro tests*. Spot tests are very convenient techniques of detection of elements or ions (radicals) present in ores, minerals, alloys, water, soil and air samples and other complex materials. Spot tests conducted on filter paper are advantageous in many respects:

- (i) offer unexpectedly high sensitivity,
- (ii) detection of individual components are possible in most cases,
- (iii) it is often possible to detect more than one component present in a sample by a single test (or reagent),
- (iv) it is often possible to avoid separation of one component from the other,
- (v) amount detected (detectable minimum) is so small that micro analytical goal is reached,
- (vi) operations are very clean and quick.

However, meeting the following requirements are extremely essential for obtaining correct and maximum information about the composition of a sample by spot test analysis.

- (i) Sound knowledge of chemical basis of all the reactions involved in qualitative analysis,
- (ii) Strict observance of trustworthy experimental conditions,
- (iii) Scrupulous cleanliness of the laboratory and equipment,
- (iv) Highest purity of the chemicals (reagents) to be used,
- (v) Blank runs (tests)/control experiments to ensure reproducibility and check contamination from reagents and environment.

1.2 Terminologies

Depending upon the chemical and physical properties of the reactants and products, for every chemical reaction, certain definite experimental conditions regarding temperature, medium (solvent if any) and concentration are to be maintained, otherwise the reaction does not take place at all. Therefore, any conclusion regarding the presence or absence of certain element, ion (radical) drawn from the observations from ill conducted reactions may be erroneous.

For a detectable observation in a chemical test, particularly those conducted in solutions, the concentration of the material under test should be appreciably high. At very low concentration, a particular reaction may fail to produce any observable change. Suppose a chemical test is based on the formation of a precipitate. A precipitate is formed only when the solution is saturated with the particular substance. A substance of very low solubility (*sparingly soluble*) is precipitated even from a very dilute solution of the ion to be detected. The term *sensitive* is used to indicate those reactions (tests) which can bring out detectable change at very low concentration. The smaller is the amount of the material detected, or lower is the concentration of the substance producing a detectable change, the higher is the *sensitivity* of the test. If the solubility of a precipitate is appreciable, it is precipitated only when the concentration of the particular ion in the solution is high. Consequently, sensitivity of the test will be low. In similar manner, we can judge the sensitivity of other types of reactions involved in qualitative chemical analysis, viz, colouration in solution, or on filter paper strips, colouration of flame, colouration or decolourization of reagent papers by test solutions or gases evolved from a reaction of the sample with a reagent.

Sensitivity of a chemical test may be quantitatively expressed by two inter connected terms:

- (i) *Identification limit* or *detectable minimum*, i.e. the smallest quantity of a material that can be detected by a test, with no reference to the concentration of the material,
- (ii) *Concentration limit* or *dilution limit*, i.e. the lowest concentration of the element or, ion at which it can be detected by the reaction (test), with no reference to the quantity of the material.

For expressing the sensitivity of a chemical test and also for comparing the efficiencies of different chemical tests conducted in solution, the following expression,

$$x [S] y$$

is quite useful, where, the symbols x , S and y have the following meanings:

S = technique employed for the test (reaction), i.e. reactions in test tubes, on spot plates, on filter paper strips etc.,

y = volume (in ml) of the test (sample) solution used for the test (reaction),

x = amount (in *microgram*, 10^{-6} g, γ)* of the material dissolved in volume y , which is revealable (detectable) by the particular technique S , i.e. *limit of identification*.

If the limit of identification ' x ' and the volume ' y ' of the solution used for the test are known, it is possible to state the concentration (or dilution) of the solution with respect to the material i.e. element, ion (radical) being sought or detected. This is the *concentration limit* or better in its reciprocal sense, *dilution limit* of the test. Dilution limit is expressed as the ratio $1:G$, where, G is the weight of the solvent per one part by weight of the substance or ion to be detected.

The dilution limit, the volume ' y ' of the test solution and identification limit ' x ' of a chemical test are interconnected by the following relation:

$$\text{Dilution limit } (1 : G) = 1 : \frac{\text{Volume of the test solution (in } ml)}{\text{Limit of identification (in } \gamma)} \times 10^6$$

$$(1 : G) = 1 : \frac{y \cdot 10^6}{x}$$

$$\therefore G = \frac{y \cdot 10^6}{x}$$

$$\text{or, } x = \frac{y \cdot 10^6}{G}$$

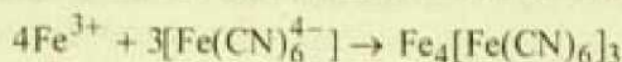
Thus, identification limit (x) of a chemical test may be calculated from the concentration (i.e. reciprocal of dilution) of the test solution and the particular volume (y) of the solution used in the test. Limit of identification of a chemical test may be determined by starting with a test solution of known concentration and systematically diluting this initial solution and

* Gama (γ) = 10^{-6} g = *microgram* μg = 0.001 mg

conducting test with the diluted solution until the solution fails to produce the detectable observation.

Examples (1.1)

- (1) To determine the sensitivity of Prussian blue test for Fe^{3+} ion, according to the reaction,



the test was conducted with a solution of $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ containing 1g of Fe^{3+} ion (i.e. 3.23g of $\text{FeCl}_3 \cdot \text{H}_2\text{O}$) per litre. The test was positive even when the solution was diluted to 400 folds, but on further dilution the test became unreliable. Find the limit of identification of Fe^{3+} and dilution limit of this reaction, if it is carried out with a drop of the solution measuring 0.05 ml in volume.

$$\text{Dilution limit} = \frac{1}{G} = \frac{\text{weight of } \text{Fe}^{3+}}{\text{weight of water}} = \frac{1}{400,000}$$

$\therefore$ 400,000 ml of the solution contains 1g of Fe^{3+}

$$\therefore 0.05 \text{ ml of the solution contains} = \frac{1 \times 0.05}{400,000} \text{ g of } \text{Fe}^{3+}$$

$$\therefore \text{Limit of identification } x = \frac{\text{Volume} \times 10^6}{\text{Dilution limit}} = \frac{y \cdot 10^6}{G}$$

$$\begin{aligned} \therefore x &= \frac{1 \times 0.05 \times 10^6}{400,000} \mu\text{g of } \text{Fe}^{3+} \\ &= 0.125 \mu\text{g of } \text{Fe}^{3+} = 0.125\gamma \text{ of } \text{Fe}^{3+} \end{aligned}$$

- (2) Identification limit for nickel by the dimethylglyoxime test is 2.8 $\mu\text{g}/2 \text{ ml}$. What is the dilution limit of the test?

$$\text{Dilution limit (G)} = \frac{\text{Vol(ml)} \times 10^6}{\text{Wt.}(\mu\text{g})} = \frac{2 \times 10^6}{2.8} = 714,286$$

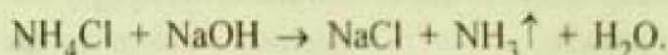
$\therefore$ Dilution limit is 1 : 714,286 i.e., 1 in 714,286.

Sensitivity of chemical tests vary within wide limits depending upon the technique and methodology applied in conducting the test, and also on the presence or absence of certain extraneous materials, which may influence the solubility of a precipitate or provide proper back ground or surface, suitable for a particular reaction (test). As for example, addition of non-electrolyte or relatively non-polar solvent such as alcohol to water, lowers the solubility of ionic solutes in water. With reactions of higher sensitivity, it is possible to detect very small amounts of various ions even using smaller volumes of the test solutions. Of course, with too high sensitivity, there is danger of being mistaken by the traces of contamination in the reagents, of the ion being detected. The problem may be overcome by performing *blank tests* under the same condition adding all the reagents except the test solution.

In addition to sensitivity, the *specificity* of a reaction (test) has great significance in qualitative analysis. Reaction of a reagent which under a particular experimental condition indicates only one substance is called *specific*, whereas, those which indicate a comparatively smaller number of substances are classified as *selective*. There are many reactions (reagents) which are more or less selective, whereas, a reaction (reagent) may be either specific or non-specific. Specific reactions are not very numerous, whereas, selective reactions are more common.

Examples (1.2)

- (1) Evolution of NH_3 on heating ammonium salts with caustic alkali is a *specific* test for NH_4^+ , since no other radical except NH_4^+ evolve NH_3 on heating with caustic alkali,



- (2) When nitrate, nitrite and ammonium salts are heated with caustic alkali in presence of Zn or Al metal, ammonia is evolved (*cf. Sects 4.24, 5.1, 5.2 and 6.11*). In this test, nitrate (NO_3^-) and nitrite (NO_2^-) ions are reduced by Zn/Al metals to NH_3 . NH_4^+ -salts on reaction with alkali also evolve NH_3 gas. Thus, this reaction is not specific for either of the three ions NO_3^- , NO_2^- and NH_4^+ , although it may be regarded as a selective reaction (test) for NH_4^+ , NO_3^- and NO_2^- ions.

Sensitivity of many reactions in qualitative analysis are often greatly increased by the utilization of *catalytic actions* and *induced reactions*, produced by very small quantities of some other substances. However, these are limited to some definite reaction systems only. Such catalytic actions obviously possess specificity and sensitivity.

Examples (1.3)

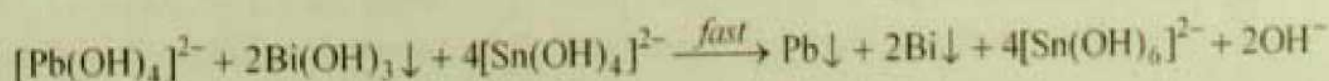
- (1) *Iodine-azide test for alkali sulfide, thiosulfate and thiocyanate*

The brown colour of iodine solution in KI is slowly decolourised in the presence of sodium azide (NaN_3) with evolution of N_2 gas,



On addition of even trace amounts of alkali sulfide, thiosulfate or thiocyanate, the above reaction is catalysed and the iodine colour is instantaneously discharged with effervescence due to evolution of N_2 gas.

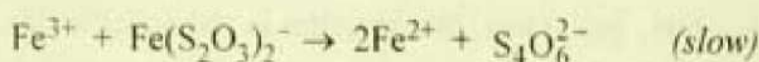
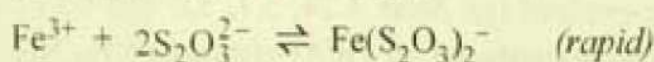
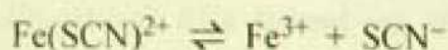
- (2) Tetrahydroxoplumbate (II) ion, $[\text{Pb}(\text{OH})_4]^{2-}$, is so slowly reduced by tetrahydroxostannate (II), $[\text{Sn}(\text{OH})_4]^{2-}$ ion, that the black precipitate of metallic lead is not observable even within an hour. In presence of traces of bismuth salt, however, the reaction is greatly accelerated, at the same time metallic bismuth is also precipitated as finely divided black material.



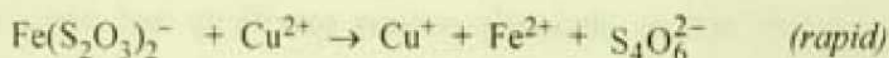
This is not exactly a catalytic reaction, it is actually an *induced reaction*, since the inducer (Bi^{3+}) ion is also used up in the course of the reaction and is not regenerated as in a catalytic reaction.

- (3) Blood red colour of the complex, $\text{Fe}^{\text{III}}(\text{SCN})^{2+}$ ion, is slowly discharged on addition of alkali thiosulfate. The reaction rate is highly accelerated in presence of traces of Cu^{II} salt, and instantaneous decolourization of the red colour takes place.

The blood red coloured complex, $\text{Fe}(\text{SCN})^{2+}$ ion, very slightly dissociates to produce small amounts of Fe^{3+} and SCN^- ions. Fe^{3+} ion rapidly reacts with thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ion to produce a transient deep violet coloured complex, $\text{Fe}(\text{S}_2\text{O}_3)_2^-$ ion, which, however, reacts with Fe^{3+} ion quite slowly.



In presence of traces ($\sim 1\gamma$) of Cu^{2+} ion, the last reaction is accelerated, as Cu^{2+} is reduced to Cu^+ by coordinated $\text{S}_2\text{O}_3^{2-}$ ion, which also reduces the Fe^{3+} in the complex, $\text{Fe}(\text{S}_2\text{O}_3)_2^-$ ion, to free Fe^{2+} ion,



Cu^+ thus produced, reduces Fe^{3+} ion extremely rapidly and itself is oxidized back to Cu^{2+} .



Since Cu^{2+} is regenerated, this reaction can be called as a *catalytic reaction*.

- (4) Redox reaction between methylene blue and hydrazine is immeasurably slow. In presence of molybdate (MoO_4^{2-}) ion, the reaction takes place extremely rapidly and the blue colour of methylene blue is discharged instantaneously. The basis of this catalytic reaction is that, hydrazine first reduces Mo^{VI} (in MoO_4^{2-} ion) to Mo^{V} which reduces methylene blue to methylene white and itself is reoxidized back to Mo^{VI} , which is again reduced to Mo^{V} by hydrazine. (cf. Sect. 8.8)

- (5) Reduction of malachite green to colourless leuco malachite green by Ti^{III} -chloride is very slow. The reaction is accelerated in presence of tungstate (WO_4^{2-}) ion. The basis of catalytic action of W^{VI} is that, W^{VI} is first reduced by Ti^{III} to W^{V} , which quickly reduces malachite green to leuco malachite green and itself is reoxidized to W^{VI} , which is again reduced by Ti^{III} .

1.3 Methods of Semi-Micro Tests

Semimicro tests may be applied in a number of different ways. The choice of procedure for a particular test (reaction) depends upon the sample, nature of the reagent and properties of the reactant ions and the products formed. Following procedures are commonly applied in conducting semi-micro tests:

- (i) Bringing together one drop of the test solution and one drop of the reagent solution on a filter paper strip or on a spot plate or on a glass plate or a porcelain crucible.
- (ii) Filter paper or asbestos or gelatine, impregnated with the reagent solution, is treated with a drop of the test solution.
- (iii) One drop of the reagent solution is brought into contact with the powdered solid sample or evaporation or ignition residue.
- (iv) Gaseous product liberated due to some reaction with the solid sample or test solution is subjected to action with a drop of the reagent or a strip of reagent paper.
- (v) One drop of the test solution is added to a large volume (0.5 - 2 ml) of the reagent solution and finally the product is extracted with an organic solvent immiscible with water.

It is found that tests carried out on filter paper show higher sensitivity than the same tests carried out in test tubes.

Examples (1.4)

- (1) Dimethylglyoxime test for Ni(II) when carried out in a test tube shows an identification limit of $2.8 \mu\text{g}/2 \text{ ml}$ and a dilution limit of around 1 : 700,000. But when the same test is carried out on a filter paper strip, it shows an identification limit of $0.015 \mu\text{g}/0.05 \text{ ml}$ and dilution limit of 1 : 3300,000.
- (2) Dilution limits of Prussian blue reaction of Fe(III) with ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$ ion, is 1 : 400,000 when conducted in a test tube and 1 : 700,000, when conducted on a filter paper.

There are even some tests which are positive when carried out on a filter paper, but are negative when carried out in a test tube:

Examples (1.5)

- (1) Benzidine blue test for Mn(II) (*cf.* Sect. 4.16)
- (2) $[\text{Fe}^{\text{II}}(\text{bipy})_3]\text{I}_2$ test for Cd(II) (*cf.* Sect 4.7)

In some tests, the filter paper itself functions as a reagent.

Examples (1.6)

Detection of traces of permanganate MnO_4^- in alkali chromate (CrO_4^{2-}) is possible by spot test on a filter paper. When a drop of a solution containing a mixture of KMnO_4 and K_2CrO_4 is placed on a filter paper strip, MnO_4^- ion, due to its high oxidation power (*cf. Ch. -2*), oxidizes the cellulose materials of the filter paper and itself is reduced to brown coloured

hydrated oxide, $\text{MnO}_2 \cdot \text{H}_2\text{O}$, which is deposited on the filter paper. On the other hand CrO_4^{2-} , due to its lower oxidizing power, does not react with the filter paper, and can be washed out by water. This permits the detection of 0.3γ of KMnO_4 in presence of as high as $20,000\gamma$ of K_2CrO_4 .

Much higher sensitivity may be achieved in spot tests using filter paper impregnated with the water soluble reagent or using a water insoluble reagent or using a water insoluble reagent acting as an ion donor.

Examples (1.7)

Test sample	Reagent	Identification limit (γ)
(1) Cu^{II}	$\text{K}_4[\text{Fe}(\text{CN})_6]$ (solution)	0.5
	$\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ (solid)	0.05
(2) $\text{Cd}(\text{II})$	Na_2S (solution)	6.3
	ZnS (solid)	0.05
(3) $\text{Mo}(\text{VI})$	Potassium ethylxanthate (solution)	0.2
	Zinc-bis(ethylxanthate) (solid)	0.01

Sensitivity and specificity of spot tests on filter paper can be further improved by applying *chromatographic* and *ion-exchange* separations and *electrophoresis* techniques. Filter paper impregnated with acidic or basic alumina can accomplish the same type of chromatographic separation as done with alumina columns. Cations and anions are fixed at separate zones of the paper when a solution containing them are allowed to ascend a strip of alumina paper. Finally the adsorptively separated materials may be detected by developing the separated zones using suitable reagents. Efficiency of *paper chromatographic separation* can be further improved by applying electrophoresis technique. In presence of a suitable reagent, if some of the constituents of a sample exist as cationic species, some constituent as anionic species and some other constituent form electroneutral species, then during electrophoresis, using a horizontal filter paper strip soaked in the reagent solution, the cationic species move toward the negative electrode (*cathode*), anionic species move toward the positive electrode (*anode*) whereas, the electroneutral species do not move on either side, but remain fixed at the centre, at the point of application of the test solution on the filter paper. Applying mutually perpendicular electric and magnetic fields, separation may be created among the metal ions of same charge but differing in the number of unpaired electrons. Metal ions with highest number of unpaired electrons are most strongly paramagnetic and are most strongly attracted by the applied magnetic field. As a result, the paramagnetic ions move slowly over the horizontal filter paper strip in the particular electric and magnetic fields. This technique is very useful in the separation between transition and non-transition metal ions, separation among transition metal ions of same or different charge types but differing in the number of unpaired electrons, which are responsible for the magnetic properties of a metal ion.

It, therefore, appears that spot tests are very useful for preliminary examinations, which should be carried out before proceeding to systematic analysis of cations and anions. The radicals indicated in the *preliminary tests* are to be complemented by *wet tests* and confirmed by *unambiguous confirmatory tests*. The preliminary tests are useful tools in obtaining general information regarding the nature of the sample. These results are important in establishing the presence or absence of certain substances, in making intelligent choice of solvents etc. Spot reactions are often successfully applied directly on the solid sample or to the solution of the sample or on the evaporation residue of the liquid samples.

CHAPTER - 2

Theoretical Basis of Qualitative Inorganic Analysis

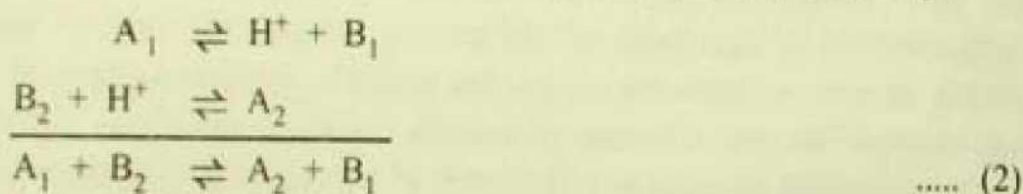
2.1 Acid-Base Equilibria in Aqueous Solution

(a) Brønsted-Lowry Concept

According to Brønsted-Lowry concept, an acid (A) is a substance that can donate a proton (H^+) and a base (B) is a substance, that can accept a proton:

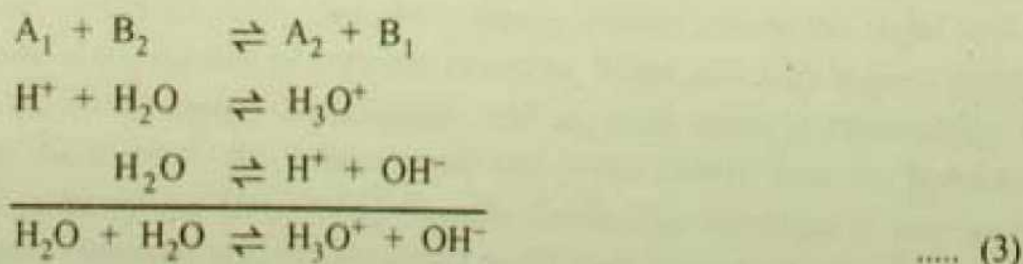


The deprotonated component, B, is called the *conjugate base* of the acid, A. Similarly, the protonated component, A, is called the *conjugate acid* of the base B. In fact, an acid (A_1) can show its proton donor property (acidic reaction) only when there is a proton acceptor (base, B_2), similarly a base (B_2) can show its proton acceptor property (basic reaction) only in the presence of a proton donor (acid, A_1). In other words, each acid-base reaction involves a pair of acids and a pair of bases, i.e., two acid-base pairs (A_1, B_1 and A_2, B_2):



The acid A_1 may be considered as a strong acid, if its proton donor ability is stronger than the proton acceptor ability of its conjugate base B_1 . Similarly, the base B_2 may be considered as a strong base if its proton acceptor ability is stronger than the proton donor ability of its conjugate acid A_2 . Thus, of the two acid-base pairs involved in an acid-base reaction (2), the stronger components of the two pairs react and the weaker components of the two pairs are formed.

Liquid water $H_2O(l)$, because of its *amphoteric* nature, can act as a proton acceptor, as well as a proton donor.



Thus, equilibrium (3) may be called as the *autoprotolytic equilibrium of water*.

The H_3O^+ ion and OH^- ions are further solvated, $[H(H_2O)_n]^+$, $n = 1 - 6$, and the process

is so rapid ($\sim 10^{-13}$ s) that the equilibrium is established instantaneously. The equilibrium constant (K) for *autoprotolysis* of water may be defined as,

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The molar concentration of water is very large compared to the concentrations of H_3O^+ and OH^- ions, [since, density of water $\approx 1 \text{ g.ml}^{-1}$, therefore, 1000 ml of water $\approx 1000 \text{ g}$ of H_2O . Hence $[\text{H}_2\text{O}(l)] = (1000/18) = 55.5 \text{ mol.lit}^{-1}$.]

So, ionization of water according to equilibrium (3) can hardly alter the concentration of H_2O molecules, which practically remains constant and it is possible to define *ionic product of water* (K_w) as a constant.

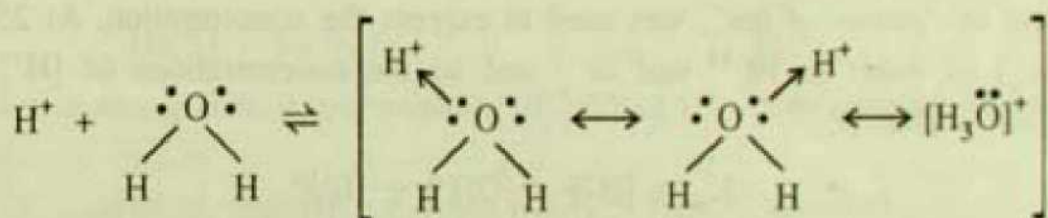
$$K_w = K [\text{H}_2\text{O}]^2 = [\text{H}_3\text{O}^+][\text{OH}^-] \text{ mol}^2.\text{lit}^{-2}.$$

Like all equilibrium constants, the value of K_w also depends upon temperature:

Temperature ($^\circ\text{C}$):	0	25	100
$K_w \times 10^{14} (\text{mol}^2.\text{lit}^{-2})$:	0.69	1.00	47.6

At any temperature, $[\text{H}_3\text{O}^+] = [\text{OH}^-]$. At 25°C , $K_w = 10^{-14} \text{ mol}^2.\text{lit}^{-2}$, therefore, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7} \text{ mol.lit}^{-1}$.

When the proton donor ability of a solute is stronger than that of water, the proton released by the solute is stabilized in the form of *hydronium ion* (H_3O^+) or, hydrated proton, through coordinate bond formation between the bare proton (H^+) and the lone pair of electrons on the O-atom of H_2O molecule.



Such solutes act as acids in water. When the proton acceptor ability of a solute is stronger than that of OH^- ion (conjugate base of H_2O), the solute deprotonates water and shows basic reaction. Strong acids are completely deprotonated (i.e. ionized) in water and molar concentration of H^+ , i.e. H_3O^+ ion, produced in solution is equal to the analytical concentration of the acid present in the solution. Similarly strong bases are completely protonated by water, and molar concentration of OH^- ion is equal to the analytical concentration of the base present in the solution.

Example (2.1) (i) Strong acids : HClO_4 , HNO_3 , HCl , H_2SO_4 .

(ii) Strong bases : NaOH , KOH , CaO , $\text{Ba}(\text{OH})_2$, etc.

Weak acids are partially deprotonated (i.e. ionized) and the weak bases are partially protonated by water.

Example (2.2)

- (i) Weak acids: HF, HCN, H₂S, H₂CO₃, H₂C₂O₄, H₃PO₄, CH₃COOH etc.
 (ii) Weak bases: NH₃, amines etc.

When a weak acid (HA) is dissolved in water, a deprotonation equilibrium,



is established. The acidity of the solution depends upon the extent of deprotonation (i.e., *degree of ionization*) and may be measured by the *activity* (concentration in dilute solution) of proton i.e. hydrogen ion at equilibrium for a given analytical concentration of the acid solution.

Similarly when a weak base such as NH₃ is dissolved in water, a protonation equilibrium,



is established. The basicity (i.e. alkalinity) of the solution, is measured by the activity (concentration in dilute solution) of OH⁻ ion in the solution at equilibrium for a given analytical concentration of the solution of the base.

(b) The pH-Scale

Danish biochemist S.P.L. Sørensen (1909) introduced a Universally used measure (scale) of hydrogen ion activity (a_{H^+}) (concentration [H⁺] in case of dilute solutions),

$$pH = -\log_{10} a_{H^+}$$

$$\text{i.e., } pH = -\log_{10} [H^+] \text{ (for dilute solution).}$$

The symbol pH, originated from the French clause, "*puissance d'hydrogene*", meaning the exponent or "*power of ten*", was used to express the concentration. At 25°C the ionic product (K_w) of water is $10^{-14} \text{ mol}^2 \cdot \text{lit}^{-2}$ and so the concentrations of $[H^+] = [OH^-] = 10^{-7} \text{ mol} \cdot \text{lit}^{-1}$. That is,

$$K_w = [H^+] \times [OH^-] = 10^{-14}$$

$$[H^+] = [OH^-] = 10^{-7}$$

For pure water at 25°C,

$$\therefore pK_w = p[H] + p[OH] = 14,$$

$$p[H] = p[OH] = 7 \text{ (neutral)}$$

At 100°C, $K_w = 4.76 \times 10^{-14}$, $pK_w = 12.32$, $p[H] = p[OH] = 6.16$ (neutral).

The pH scale is meant for expressing H⁺ ion concentration of dilute solutions of acids and bases ranging from 1(M) solution of a strong acid ($[H^+] = 1(M)$) to 1(M) solution of a strong base ($[OH^-] = 1(M)$). At 25°C, since, $pK_w = p[H] + p[OH] = 14$, and $p[H] = p[OH] = 7$, the pH scale extends from pH = 0 to pH = 14, corresponding to $[H^+] = 1(M)$ to $[OH^-] = 1(M)$, respectively.



1(M) strong acid	Neutral water	1(M) strong base
$[H^+] = 1\text{ M}$	$[H^+] = [OH^-] = 10^{-7}\text{ M}$	$[OH^-] = 1\text{ M}$
pH 0	7	14
pOH 14	7	0

As the strong acids and strong bases are completely ionized, $p[H]$ and $p[OH]$ of their dilute solutions may be directly obtained from the negative logarithm to base 10 of their analytical concentrations.

Example (2.3) At 25°C ,

Concentration (M) :	1	0.1	0.01	0.001	0.0001
pH (Strong acid) :	0	1	2	3	4
pH (Strong base) :	14	13	12	11	10

Examples (2.4) pH of solutions of strong acids:

(1) Find the $p[H]$ of an aqueous solution of $2 \times 10^{-4}\text{M}$ HNO_3 .

HNO_3 is a strong acid. It ionizes completely, so that, $[H^+] = [\text{HNO}_3] = 2 \times 10^{-4}\text{M}$

$$\therefore p[H] = -\log[H^+] = -\log(2 \times 10^{-4}) = 3.699 \approx 3.70$$

(2) 0.1 ml of 10^{-4}M aqueous solution of HCl is diluted to 1000 ml. What will be the pH of the resulting solution at 25°C ?

If the final concentration of acid in the diluted solution be $[\text{HCl}]$, then,

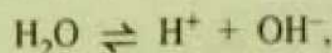
$$[\text{HCl}] \times 1000 = 0.1 \times 10^{-4}\text{M}$$

$$\therefore [\text{HCl}] = 10^{-8}\text{M}$$

Since HCl is a strong acid, it will produce 10^{-8}M of H^+ ion in aqueous solution. But in this case,

$$p[H] = -\log[H^+] \neq (-\log[\text{HCl}] = 8) \text{ (i.e., alkaline).}$$

Because of autoionization of H_2O molecules in liquid water according to,



for which, $K_w = [H^+] \times [OH^-] = 10^{-14}$ (at 25°C)

and $[H^+] = [OH^-] = 10^{-7}$ ($\therefore 1 : 1$ electrolyte),

10^{-7}M of H^+ ion is expected to be already present in liquid water at 25°C . In the presence of HCl , an additional amount (10^{-8}M) of H^+ ions are introduced into the solution. But the total concentration of H^+ ion is not just $[10^{-7}\text{M} + 10^{-8}\text{M}]$, since in the presence of completely ionized HCl , the ionization of H_2O is depressed due to *common ion effect* by H^+ ion. If in the diluted solution, the concentration of the completely ionized strong acid = $A\text{M}$, then the total concentration of H^+ ion will be given by,

$$[H^+] = A + [OH^-] \text{ (due to ionization of } H_2O)$$

$$= A + \frac{K_w}{[H^+]}$$

$$\text{or, } [H^+]^2 - A[H] - K_w = 0$$

$$\therefore [H^+] = \frac{A \pm \sqrt{A^2 + 4K_w}}{2}$$

$$\text{Here, } A = 10^{-8}, K_w = 10^{-14}, \therefore \sqrt{A^2 + 4K_w} = 20.025 \times 10^{-8}$$

$$\therefore [H^+](-) = \frac{A - \sqrt{A^2 + 4K_w}}{2} = \frac{10^{-8} - 20.025 \times 10^{-8}}{2} = \text{Negative value (absurd)}$$

$$[H^+](+) = \frac{A + \sqrt{A^2 + 4K_w}}{2} = \frac{10^{-8}(1 + 20.025)}{2} = 10.5125 \times 10^{-8} M$$

$$\therefore p[H] = -\log[H^+] = -\log(10.5125 \times 10^{-8}) = 6.978 \approx 6.98$$

(c) Aqueous Solutions of Weak Acids and Weak Bases

Since the weak acids and weak bases are only partly deprotonated and protonated in aqueous solution, $p[H]$ of such solutions can not be directly calculated from negative logarithm of analytical concentrations of these materials. Acidity or alkalinity of such solutions depends upon the degree or extent of deprotonation (for acids) and protonation (for bases) i.e., ionization of the substances at equilibrium at a particular temperature.

(i) Weak acid solutions

Deprotonation (i.e ionization) equilibrium of a weak acid (HA) may be expressed as,



According to *Ostwald dilution law*, the deprotonation constant (i.e, ionization constant), K_a , for such an equilibrium is defined according to,

$$K_a = \frac{[H^+][A^-]}{[HA]} \dots\dots (2)$$

As HA is an 1:1 electrolyte, $[H^+] = [A^-]$. If C be the initial analytical concentration of HA, then at equilibrium,

$$C = [HA] + [A^-] = [HA] + [H^+]$$

$$\therefore [HA] = C - [H^+].$$

$$\therefore K_a = \frac{[H^+]^2}{C - [H^+]} \dots\dots (3)$$

Moderately weak acids are appreciably deprotonated (i.e, ionized). H^+ ion concentration of such solutions may be calculated by solving the quadratic equation (4):

$$[H^+]^2 + K_a[H^+] - K_aC = 0 \dots (4)$$

obtained on simplification of the equation (3) neglecting the negative value of the root. For a very weak acid, for which deprotonation (ionization) is almost negligible,

$$[H^+] \ll C$$

$$\therefore C - [H^+] \approx C$$

$$K_a = \frac{[H^+]^2}{C} \dots (5)$$

$$\therefore pH = \frac{1}{2} pK_a - \frac{1}{2} \log C \dots (6)$$

Examples (2.5)

- (1) Find the pH of a 0.02 M aqueous solution of acetic acid ($K_a = 1.8 \times 10^{-5}$ at $25^\circ C$).

This is a sufficiently weak acid, $C = 0.02$ M,

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.74$$

$$pH = \frac{1}{2} pK_a - \frac{1}{2} \log C$$

$$= \frac{1}{2} \times 4.74 - \frac{1}{2} \log(0.02) = 2.37 - \frac{1}{2}(-1.70) = 2.37 + 0.85 = 3.22$$

Considering acetic acid as a moderately weak acid, if the $[H^+]$ ion concentration is calculated using the quadratic equation (4),

$$[H^+]^2 + K_a[H^+] - K_aC = 0 \dots (4)$$

$$\text{then, } [H^+](-) = \frac{-K_a - \sqrt{K_a^2 + 4K_aC}}{2} = \text{Negative (absurd)}$$

$$[H^+](+) = \frac{-K_a + \sqrt{K_a^2 + 4K_aC}}{2}$$

$$\therefore K_a = 1.8 \times 10^{-5}, C = 0.02 \text{ (M)},$$

$$\therefore K_a^2 = (1.8 \times 10^{-5})^2 = 3.24 \times 10^{-10}$$

$$4K_aC = 4 \times 1.8 \times 10^{-5} \times 0.02 = 1.44 \times 10^{-6}$$

$$\sqrt{K_a^2 + 4K_aC} = 1.2 \times 10^{-3}$$

$$\therefore [H^+](+) = \frac{-1.8 \times 10^{-5} + 1.2 \times 10^{-3}}{2} = 5.91 \times 10^{-4}$$

$$\therefore pH = -\log[H^+] = -\log(5.91 \times 10^{-4}) = 3.228 \approx 3.23$$

Thus, acetic acid is a sufficiently weak acid, so that, $[H^+] \ll C$ at equilibrium, is a valid approximation.

- (2) Calculate the pH of a 0.02 M aqueous solution of monochloroacetic acid ($pK_a = 2.63$, at 25°C).

$$pK_a = 2.63, C = 0.02 \text{ M}$$

$$\therefore K_a = \text{Inverse log}(-pK_a) = \text{Inverse log}(-2.63) = 2.344 \times 10^{-3}$$

Since this is a moderately weak acid, appreciably deprotonated (ie, ionized) in aqueous solution, so that, $(C - [H^+]) \neq C$. Hydrogen ion concentration of such a solution should be calculated using the quadratic equation (4):

$$[H^+]^2 + K_a[H^+] - K_aC = 0 \dots\dots (4)$$

$$[H^+](+) = \frac{-K_a + \sqrt{K_a^2 + 4K_aC}}{2} \quad (\because \text{negative root is absurd})$$

$$K_a^2 = (2.344 \times 10^{-3})^2 = 5.494 \times 10^{-6}$$

$$4K_aC = 4 \times 2.344 \times 10^{-3} \times 0.02 = 1.875 \times 10^{-4}$$

$$\sqrt{K_a^2 + 4K_aC} = 13.9 \times 10^{-3}$$

$$\begin{aligned} \therefore [H^+](+) &= \frac{-2.344 \times 10^{-3} + 13.9 \times 10^{-3}}{2} \\ &= \frac{(-2.344 + 13.9) \times 10^{-3}}{2} = 5.78 \times 10^{-3} \end{aligned}$$

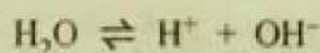
$$\therefore p[H] = -\log[H^+] = -\log[5.78 \times 10^{-3}] = 2.24$$

If the $p[H]$ of this solution is calculated assuming the acid as a sufficiently weak acid, the pH value will be slightly lower than the actual,

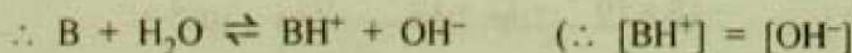
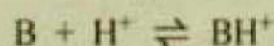
$$pH = \frac{1}{2}pK_a - \frac{1}{2}\log C = \frac{1}{2} \times 2.63 - \frac{1}{2}\log(0.02) = 2.16$$

(ii) Solutions of weak bases

In aqueous solution, weak bases (B) undergo protonation according,



$$K_w = [H^+][OH^-]$$



Deprotonation constant (K_{BH^+}) of the base cation (BH^+) may be defined as,

$$K_{BH^+} = \frac{[H^+][B]}{[BH^+]}$$

$$\therefore K_{BH^+} \cdot K_w = \frac{[H^+][B]}{[BH^+]} \times [H^+][OH] = [H^+]^2[B] = [H^+]^2 C$$

where, C = analytical concentration of the base B .

$$\therefore \frac{1}{[H^+]} = \left(\frac{C}{K_w K_{BH^+}} \right)^{\frac{1}{2}}$$

$$\therefore p[H] = \frac{1}{2} pK_w + \frac{1}{2} pK_{BH^+} + \frac{1}{2} \log C$$

Example (2.6)

(1) Calculate the pH of a $0.02 M$ solution of ammonia in water at $25^\circ C$. [Given: $pK_w = 14$,

$$pK_{NH_4^+} = 9.2]$$

$$\begin{aligned} p[H] &= \frac{1}{2} pK_w + \frac{1}{2} pK_{NH_4^+} + \frac{1}{2} \log C \\ &= \frac{1}{2} \times 14 + \frac{1}{2} \times 9.2 + \frac{1}{2} \log(0.02) \\ &= 7 + 4.6 - 0.85 = 10.75 \end{aligned}$$

(d) Buffer Solutions

Solutions of a mixture of a weak acid and one of its salts with a strong or weak base, or the solution of a mixture of weak base and one of its salts with a strong or a weak acid have the unique property of resisting the changes of pH within certain range, when small amount of an acid or a base is added to them. Such solutions are called *buffer solutions* and their property of resisting the change of pH is called *buffer action*.

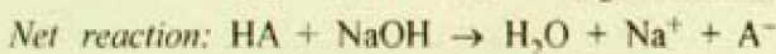
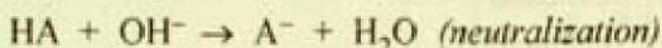
(i) Mechanism of buffer action

If to a buffer solution consisting of a weak acid (HA) and its salt (Na^+A^-) is added a small amount of a strong acid (HCl), which is completely ionized to produce the same amount of H^+ ion, the pH of the resulting solution remains practically unchanged due to buffer action, since the H^+ ions released from the strong acid (H^+Cl^-) combine with the salt anion (A^-), which is a strong base, as the conjugated acid (HA) is a weak acid that ionizes only partly.

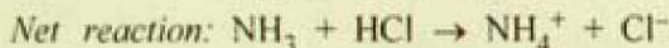
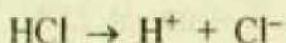


Thus, the H^+ ion concentration of the resulting solution does not increase appreciably even when small amount of a strong acid (H^+Cl^-) is added to a mixture of HA and Na^+A^- .

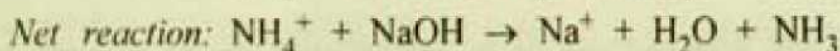
Similarly when a small amount of a strong base (NaOH) is added to the mixture of HA and NaA, the OH^- ions released from the base combine with unionized molecules of the weak acid (HA), when salt (NaA) and H_2O molecules are formed through neutralization:



If to a buffer solution composed of a weak base NH_3 and its salt NH_4Cl is added a small amount of a strong acid (HCl), then the NH_3 molecules combine with protons released from HCl.



If a small amount of a strong base (NaOH) is added to this solution, the OH^- ion released from the strong base takes up a proton from the NH_4^+ ion, which is the conjugate acid of the base NH_3 .



(ii) pH of buffer solutions

Suppose a buffer solution is composed of a weak acid (HA) and its salt (NaA) with a strong base NaOH. In aqueous solution, the weak acid HA is partially ionized,



The ionization constant K_a is defined as,

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \dots (1)$$

The salt NaA is completely ionized,



If 'a' mole of HA is mixed with 'b' mole of NaA and the resulting solution is allowed

to attain equilibrium, then, the equilibrium concentrations of unionized acid (HA) and the anion (A^-) will be given by,

$$[HA] = a - [H^+]$$

$$[A^-] = b + [H^+]$$

Substituting these values in the expression for K_a , one obtains,

$$K_a = \frac{[H^+](b + [H^+])}{(a - [H^+])} \dots\dots (3)$$

Since the acid HA is a weak acid, in presence of the completely ionized salt (NaA), ionization of this acid will be greatly depressed due to common ion effect of A^- ion, so that, without any serious error, the equilibrium concentrations of unionized acid, HA and the salt anion, A^- may be taken as,

$$[HA] \approx a \text{ (i.e., analytical concentration of the weak acid)}$$

$$[A^-] \approx b \text{ (i.e., analytical concentration of the salt). Therefore,}$$

$$K_a = \frac{[H^+]b}{a}$$

$$\text{or, } \frac{1}{[H^+]} = \frac{1}{K_a} \cdot \frac{b}{a}$$

$$\therefore p[H] = pK_a + \log \frac{b}{a}$$

$$\text{i.e., } p[H] = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \dots\dots (4)$$

This expression is the well known *Handerson-Hasselbalch equation*.

$p[H]$ of a buffer solution composed of equimolar concentrations of an acid and its salt, is exactly equal to pK_a of the acid, i.e when, $[\text{Acid}] = [\text{Salt}]$

$$p[H] = pK_a \dots\dots (4a)$$

If a small amount ($x \text{ mol.lit.}^{-1}$ provided $x \ll a$, $x \leq b$) of a strong acid (HCl) is added to this buffer mixture, then due to buffer action, the equilibrium concentrations of HA and A^- become,

$$[A^-] = (b - x)$$

$$[HA] = (a + x)$$

and pH of the buffer solution at this condition will be,

$$p[H] = pK_a + \log \frac{(b - x)}{(a + x)} \dots\dots (4b)$$

Similarly if the same ($x \text{ mol.lit.}^{-1}$) amount of a strong base (NaOH) is added to this buffer mixture, the equilibrium concentrations of HA and A^- become,

$$[\text{HA}] = a - x$$

$$[\text{A}^-] = b + x$$

and $p[\text{H}]$ of the buffer solution under this condition is given by,

$$p[\text{H}] = pK_a + \log \frac{(b + x)}{(a - x)} \dots (4c)$$

If a buffer solution is diluted, its $p[\text{H}]$ remains practically unchanged, as the ratio of equilibrium concentrations of the unionized acid, HA, and the completely ionized salt remains unchanged.

Examples (2.7)

- (1) Find the $p[\text{H}]$ of a buffer solution composed of 0.2 M hydrofluoric acid ($pK_a = 3.2$) and 0.4 M sodium fluoride. If 50 ml of this buffer solution is diluted to 100 ml, what will be the $p[\text{H}]$ of the diluted buffer solution?

$$\begin{aligned} p[\text{H}] &= pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= 3.2 + \log \left(\frac{0.4}{0.2} \right) = 3.2 + \log 2 = 3.2 + 0.301 = 3.501 \end{aligned}$$

$$\text{Concentration of HF in the diluted solution} = \frac{50 \times 0.2}{100} \text{ M} = 0.1 \text{ M}$$

$$\text{Concentration of NaF in the diluted solution} = \frac{50 \times 0.4}{100} \text{ M} = 0.2 \text{ M}$$

$\therefore p[\text{H}]$ of the diluted buffer solution will be,

$$p[\text{H}] = 3.2 + \log \frac{0.2}{0.1} = 3.2 + \log 2 = 3.2 + 0.301 = 3.501$$

Thus, $p\text{H}$ of the buffer solution remains unchanged on dilution.

- (2) In what molar proportion should sodium acetate and acetic acid be mixed for preparing a buffer solution of $p\text{H}$ 4.5 at 25°C ? [Given for acetic acid: $K_a = 1.8 \times 10^{-5}$]

$$\therefore K_a = 1.8 \times 10^{-5}$$

$$\therefore pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

Since the buffer solution will be composed of a weak acid (acetic acid) and its salt with a strong base, the $p[\text{H}]$ of this buffer solution may be expressed by Handerson-Hasselbalch equation,

$$p[\text{H}] = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore 4.5 = 4.74 + \log \frac{[\text{acetate}]}{[\text{acetic acid}]}$$

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$$\therefore \log \frac{[\text{acetate}]}{[\text{acetic acid}]} = (4.5 - 4.74) = -0.24$$

$$\therefore \frac{[\text{acetate}]}{[\text{acetic acid}]} = \text{Inverse log}(-0.24) = 0.575$$

- (3) How much sodium acetate trihydrate and glacial acetic acid [sp. gr. = 1.044, 17.4 M] should be mixed for preparing 1 litre of a buffer solution of pH 4.5, which would be 0.5 M in acetic acid? [Given: pK_a of acetic acid = 4.74].

From previous example (2), for a buffer solution of $p[H]$ 4.5, consisting of acetic acid and sodium acetate, the molar ratio of acetate : acetic acid = 0.575,

$$\text{i.e., } \frac{[\text{Sodium acetate}]}{[\text{Acetic acid}]} = 0.575$$

$$\therefore [\text{Sodium acetate}] = [\text{Acetic acid}] \times 0.575 = 0.5 \text{ M} \times 0.575 = 0.288 \text{ M}$$

Glacial acetic acid is 17.4 M. If V ml of glacial acetic is required for 1000 ml of 0.5 M acetic acid, then,

$$V = \frac{1000 \times 0.5}{17.4} \text{ ml} = 28.7 \text{ ml}$$

Formula weight of sodium acetate trihydrate:

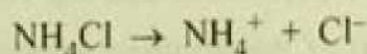
$$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O} = 12 + (1 \times 3) + 12 + (16 \times 2) + 23 + (18 \times 3) = 136$$

$$\therefore 1000 \text{ ml of } M \text{ sodium acetate} \equiv 136 \text{ g of } \text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$$

$$\therefore 1000 \text{ ml of } 0.288 \text{ M sodium acetate} \equiv 136 \times 0.288 = 39.17 \approx 39.2 \text{ g of } \text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}.$$

So, 1 litre of an acetic acid-acetate buffer solution of $p[H]$ 4.5, that is 0.5 M in acetic acid, can be prepared by dissolving ~ 39.2g of sodium acetate trihydrate in water and adding ~ 28.7 ml of glacial acetic acid into it, then diluting the mixture with water to 1 litre and mixing uniformly.

$p[H]$ of a buffer solution consisting of a weak base, NH_3 and one of its salts with a strong acid, such as NH_4Cl , can also be calculated using Handerson-Hasselbalch equation. The salt, NH_4Cl is completely ionized:



NH_4^+ ion serves as the weak acid, whereas, the Cl^- ion has practically no basic character, since it is the conjugate base of a strong acid, HCl. Thus, the combination of NH_4^+ ion derived from NH_4Cl and NH_3 forms the buffer mixture. NH_4^+ ion ionizes as a weak acid,



NH_3 added to the mixture, will combine with protons to form NH_4^+ ion. If 'a' mole of NH_4Cl is mixed with 'b' mole of NH_3 , then, after the attainment of equilibrium, the concentrations of NH_4^+ ion and NH_3 will be :

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$$[\text{NH}_4^+] = a - [\text{H}^+].$$

$$[\text{NH}_3] = b + [\text{H}^+].$$

$$\therefore K_{\text{NH}_4} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{[\text{H}^+](b + [\text{H}^+])}{(a - [\text{H}^+])}$$

Since NH_3 is a weak base, its protonation equilibrium to form NH_4^+ ion will remain greatly depressed in presence of completely ionized salt, NH_4Cl , producing NH_4^+ ions, due to common ion effect of the latter. Thus, the equilibrium concentration of NH_3 may be taken as its analytical concentration, 'b' and that of NH_4^+ ion as its analytical concentration, 'a' without any serious error.

Therefore, rearranging the expression for K_{NH_4} one obtains,

$$\frac{1}{[\text{H}^+]} = \frac{1}{K_{\text{NH}_4}} \cdot \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$\text{i.e., } p[\text{H}] = pK_{\text{NH}_4} + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$\text{or, } p[\text{H}] = pK_{\text{NH}_4} + \log \left(\frac{b}{a} \right).$$

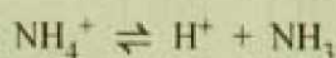
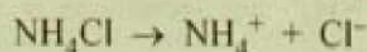
Examples (2.8)

- (1) Calculate the $p\text{H}$ of a buffer solution which is 0.5 (M) in NH_3 and 0.25 (M) in NH_4Cl .
[Given : $pK_{\text{NH}_4} = 9.26$].

$$\begin{aligned} p[\text{H}] &= pK_{\text{NH}_4} + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \\ &= 9.26 + \log \left(\frac{0.5}{0.25} \right) = 9.26 + \log 2 = 9.56. \end{aligned}$$

- (2) 5g of pure NH_4Cl salt is dissolved in water and the volume of the solution is made upto 250 ml. What will be the $p[\text{H}]$ of the resulting solution? [Given: $pK_{\text{NH}_4} = 9.26$]

Being a salt, NH_4Cl ionizes completely, producing equivalent amount of NH_4^+ ion, which ionizes in solution as a weak monoprotic acid,



$$\therefore [\text{H}^+] = [\text{NH}_3]$$

$$\text{Formula weight of } \text{NH}_4\text{Cl} = (14 + 4 + 35.5) = 53.5$$

∴ Concentration of NH_4Cl in the 250 ml solution is

$$= \frac{5 \times 1000}{250 \times 53.5} (M) = 0.374 (M)$$

$$\therefore [\text{NH}_4^+] = 0.374 (M)$$

$$\text{Now, } K_{\text{NH}_4} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{[\text{H}^+]^2}{[\text{NH}_4^+]} \quad (\because [\text{H}^+] = [\text{NH}_3])$$

$$\therefore \frac{1}{[\text{H}^+]^2} = \frac{1}{K_{\text{NH}_4}} \cdot \frac{1}{[\text{NH}_4^+]}$$

$$\therefore p[\text{H}] = \frac{1}{2} pK_{\text{NH}_4} - \frac{1}{2} \log[\text{NH}_4^+]$$

$$= \frac{1}{2} (9.26) - \frac{1}{2} \log(0.374) = 4.84$$

(3) In what molar proportion should NH_3 and NH_4Cl be mixed for preparing a buffer solution of $p[\text{H}] = 10$? [Given : $pK_{\text{NH}_4} = 9.26$]

$$p[\text{H}] = pK_{\text{NH}_4} + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$\therefore \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = (p[\text{H}] - pK_{\text{NH}_4})$$

$$\therefore \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = \text{Inverse log } (p[\text{H}] - pK_{\text{NH}_4})$$

$$= \text{Inverse log } (10 - 9.26) = 5.495 \approx 5.5$$

$$\therefore [\text{NH}_3] : [\text{NH}_4^+] = 5.5 : 1$$

(4) How much NH_4Cl and liquor ammonia [sp.gr. = 0.88, 15 M] should be mixed for preparing 1 litre of a buffer solution of $p[\text{H}]$ 10, which would be 1.3 M in NH_4Cl ? [Given: $pK_{\text{NH}_4} = 9.26$]

For a buffer solution of $p[\text{H}]$ 10 consisting of NH_3 and NH_4Cl , the molar ratio of $([\text{NH}_3]/[\text{NH}_4^+]) = 5.5$ [see the solution of example (3)]

Since, $[\text{NH}_4^+] = [\text{NH}_4\text{Cl}] = 1.3 \text{ M}$,

$$\therefore [\text{NH}_3] = [\text{NH}_4^+] \times 5.5 = 1.3 \text{ M} \times 5.5 = 7.15 \text{ M}$$

Volume (V) of liquor ammonia required:

$$1000 \text{ ml of } 7.15 \text{ M } \text{NH}_3 \equiv V \text{ ml of } 15 \text{ M liquor } \text{NH}_3.$$

$$\therefore V = \frac{1000 \times 7.15}{15} = 476.7 \text{ ml of liquor } \text{NH}_3.$$

$$1000 \text{ ml of } 1.3 \text{ (M) } \text{NH}_4\text{Cl} \equiv (53.5 \times 1.3)\text{g of } \text{NH}_4\text{Cl} \\ = 69.6 \text{ g of } \text{NH}_4\text{Cl}.$$

Note: Concentration of NH_3 in commercial liquor ammonia solution may be lower than 15 M due to volatile nature of ammonia. So, while preparing a $\text{NH}_3 - \text{NH}_4\text{Cl}$ buffer solution, the amount of ammonia should be judged on the basis of its actual concentration in liquor ammonia.

(iii) Buffer capacity

The ability of a buffer solution to maintain a nearly fixed pH is called its *buffer capacity*. Buffer capacity is a measure of the amount of acid or base that the buffer solution can absorb without a significant change in its pH. In opposite sense, it is also a measure of the changes in pH on addition of a given amount of acid or base. Obviously buffer capacity depends upon the number of moles of the weak acid and its salt (i.e. conjugate base) or of the weak base and its salt (i.e. conjugate acid) present in the mixture. The greater are the concentrations of the two components the higher is the buffer capacity. A buffer solution shows its maximum buffer capacity when it is composed of equimolar concentrations of the weak acid and its conjugate base (i.e. salt) or of the weak base and its conjugate acid (i.e. salt), i.e. when $p[\text{H}]$ of the buffer solution is equal to pK_a of the weak acid it is composed of.

Example (2.9)

(1) 0.1 M of each of hydrochloric acid and sodium hydroxide solutions were separately added to the three acetic acid (HAc) - sodium acetate (NaAc) buffer solutions of following compositions:

$$(i) [\text{HAc}] = 1.0 \text{ M} + [\text{NaAc}] = 1.0 \text{ M}$$

$$(ii) [\text{HAc}] = 1.0 \text{ M} + [\text{NaAc}] = 0.25 \text{ M}$$

$$(iii) [\text{HAc}] = 0.25 \text{ M} + [\text{NaAc}] = 1.0 \text{ M}$$

Calculate the $p[\text{H}]$ of the buffer solutions (i – iii) before and after addition of the acid and base solutions. Hence indicate the buffer solution of the highest buffer capacity. [Given pK_a of HAc = 4.74].

$p[\text{H}]$ of the buffer solutions (i-iii) before addition of the acid and base:

$$p[\text{H}] = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore p[\text{H}](i) = 4.74 + \log \frac{1.0}{1.0} = 4.74 + 0 = 4.74$$

$$p[\text{H}](ii) = 4.74 + \log \frac{0.25}{1.0} = 4.74 - 0.60 = 4.14$$

$$p[\text{H}](iii) = 4.74 + \log \frac{1.0}{0.25} = 4.74 + 0.60 = 5.34$$

$p[\text{H}]$ values after addition of 0.1 M HCl ($[\text{H}^+] = 0.1 \text{ M}$):

$$p[H] \text{ (i)} = 4.74 + \log \frac{1.0 - 0.1}{1.0 + 0.1} = 4.74 + \log \frac{0.9}{1.1} = 4.74 - 0.09 = 4.65$$

$$p[H] \text{ (ii)} = 4.74 + \log \frac{0.25 - 0.1}{1.0 + 0.1} = 4.74 + \log \frac{0.15}{1.1} = 4.74 - 0.87 = 3.87$$

$$p[H] \text{ (iii)} = 4.74 + \log \frac{1.0 - 0.1}{0.25 + 0.1} = 4.74 + \log \frac{0.9}{0.35} = 4.74 + 0.41 = 5.15$$

$p[H]$ values after addition of 0.1 M NaOH ($[OH^-] = 0.1 M$):

$$p[H] \text{ (i)} = 4.74 + \log \frac{1.0 + 0.1}{1.0 - 0.1} = 4.74 + \log \frac{1.1}{0.9} = 4.74 + 0.09 = 4.83$$

$$p[H] \text{ (ii)} = 4.74 + \log \frac{0.25 + 0.1}{1.0 - 0.1} = 4.74 + \log \frac{0.35}{0.9} = 4.74 - 0.41 = 4.33$$

$$p[H] \text{ (iii)} = 4.74 + \log \frac{1.0 + 0.1}{0.25 - 0.1} = 4.74 + \log \frac{1.1}{0.15} = 4.74 + 0.87 = 5.61$$

The results are summarised below:

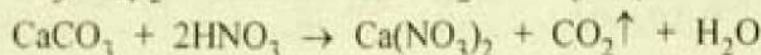
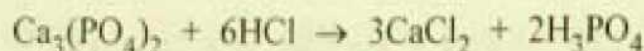
Buffer solutions	(i)	(ii)	(iii)
$\frac{[Salt]}{[Acid]} = \frac{[Ac^-]}{[HAc]}$	1:1	0.25 : 1 = 1 : 4	1 : 0.25 = 4 : 1
$p[H]$	4.74	4.14	5.34
$p[H]$ after addition of 0.1 M HCl	4.65	3.87	5.15
0.1 M NaOH	4.83	4.33	5.61
Change of $p[H]$ on addition of 0.1 M base or acid	± 0.09	± 0.27	$\pm (0.19 \text{ to } 0.27)$

It is evident from this example that on addition of a given amount of strong acid or a strong base, the maximum resistance to change of $p[H]$ is offered by buffer solution (i) which contains equimolar concentrations of the weak acid and its salt (i.e. conjugate base), and $p[H]$ of this solution is equal to pK_a of the weak acid (HAc) it is composed of.

(e) Polyprotic Acids and Their Salts

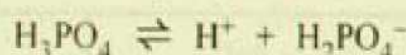
In qualitative inorganic analysis we often come across metal salts of polyprotic acids, eg. phosphates, arsenates, carbonates, sulfides, sulfites, sulfates etc. Most polyprotic acids are weaker acids than hydrochloric acid or nitric acid, which are employed for dissolution of the samples. On dissolution of these salts in dilute HCl or HNO_3 , the polyprotic acids are liberated and remain

in solution, whereas, the metal ions remain in solution as their chlorides or nitrate salts as the case may be.



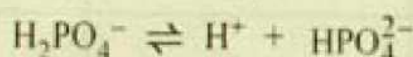
During routine analysis, depending upon $p[\text{H}]$ of the solutions, these polyprotic acids undergo deprotonation, forming the corresponding anions, which greatly influence the solution $p[\text{H}]$. Since the polyprotic acids are in general weak acids, their anions are strong bases (conjugate bases), which may combine with metal ions in solution, causing precipitation of metal salts (or basic salts) of the polyprotic acids and even metal hydroxides, thereby, may interfere the detection and separation of the metal ions. It is often necessary to remove these polyprotic acid anions from the test solutions prior to separation and, or, identification of certain metallic ions. Knowledge of the deprotonation equilibria of the polyprotic acids and $p[\text{H}]$ of the solutions containing polyprotic acids and their acid-salts and normal salts helps us setting up the experimental conditions required for detection and separation of metal ions in solution during qualitative inorganic analysis.

Let us consider the protonation - deprotonation equilibria with orthophosphoric acid, H_3PO_4 , which is a triprotic acid. H_3PO_4 undergoes three successive steps of ionization:



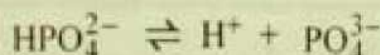
$$K_{a3} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3} \text{ (at } 25^\circ\text{C)}$$

$$\therefore pK_{a3} = 2.12$$



$$K_{a2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 6.2 \times 10^{-8} \text{ (at } 25^\circ\text{C)}$$

$$\therefore pK_{a2} = 7.21$$



$$K_{a1} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = 4.8 \times 10^{-13} \text{ (at } 25^\circ\text{C)}$$

$$\therefore pK_{a1} = 12.32$$

Stepwise ionization constants of polyprotic acids decrease by a factor of $\sim 10^4$ to 10^6 in the order : $K_{a3} > K_{a2} > K_{a1}$, because of electrostatic forces of attraction between proton and the acid anions increase with increase of anionic charge. Stepwise ionization constants (in terms of pK_{a1} values) of some common polyprotic acids are presented in Table 2:1. (see also Appendix A-1)

Table 2.1

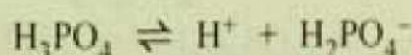
Stepwise ionization constants (interms of pK_{a1}) of some polyprotic inorganic acids at 25°C.

Acid (Formula)	pK_{a3}	pK_{a2}	pK_{a1}
Orthophosphoric acid (H_3PO_4)	2.12	7.21	12.32
Carbonic acid (H_2CO_3)	–	6.37	10.25
Sulfurous acid (H_2SO_3)	–	1.82	7.20
Hydrogen sulfide (H_2S)	–	7.1	~13.0
Arsenic acid (H_3AsO_4)	2.3 – 3.6	6.8 – 7.2	12.0 – 12.5
Sulfuric acid (H_2SO_4)	–	Negative	1.92
Thiosulfuric acid ($H_2S_2O_3$)	–	0.3 – 1.2	1.5
Chromic acid (H_2CrO_4)	–	0.7	6.5

Aqueous solutions of polyprotic acids contain several acid species, e.g. aqueous solution of phosphoric acid may contain H_3PO_4 , $H_2PO_4^-$, HPO_4^{2-} , PO_4^{3-} ions, as well as H_2O molecules, which participate in protonation-deprotonation equilibria, however, the $p[H]$ of the solution at a particular condition is governed by the principal reactions, as will be evident from the following considerations, with phosphoric acid and its salts.

(i) $p[H]$ of a solution of orthophosphoric acid

In aqueous solution, H_3PO_4 may undergo three steps of deprotonation equilibria as described before, apart from ionization of H_2O molecules to form H^+ and OH^- ions. But a perusal of the ionization constants (Table 2.1) of H_3PO_4 and ionic product of water ($K_w = 10^{-14}$ at 25°C) reveals that K_{a3} of H_3PO_4 is $\sim 10^5$ times larger than its K_{a2} and $\sim 10^{10}$ times larger than its K_{a1} and $\sim 10^{12}$ times larger than K_w . Thus, when H_3PO_4 undergoes deprotonation to produce $H_2PO_4^-$ ion, the deprotonation equilibria of $H_2PO_4^-$, HPO_4^{2-} and ionization equilibrium of H_2O are suppressed. That is, only the first step deprotonation equilibrium of H_3PO_4 ,



is the predominant chemical reaction, which should only be taken into consideration for calculation of $p[H]$ of the solution.

$$K_{a3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$

$$\therefore [H^+] = [H_2PO_4^-]$$

$$\therefore [H_3PO_4] = C - [H_2PO_4^-] = C - [H^+]$$

where, C = analytical concentration of H_3PO_4 in the solution. Since H_3PO_4 is a moderately weak acid, its ionization is appreciable, and it will not be correct to assume $C - [H^+] \approx C$. Therefore,

$$K_{a3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{[H^+]^2}{C - [H^+]}$$

$$\therefore [H^+]^2 + K_{a3}[H^+] - CK_{a3} = 0$$

$$\therefore [H^+] = \frac{-K_{a3} \pm \sqrt{K_{a3}^2 + 4CK_{a3}}}{2}$$

Since the negative root is improbable,

$$[H^+](+) = \frac{-K_{a3} + \sqrt{K_{a3}^2 + 4CK_{a3}}}{2}$$

$$p[H] = -\log[H^+] = \log \frac{1}{[H^+]} = \log \left(\frac{2}{-K_{a3} + \sqrt{K_{a3}^2 + 4CK_{a3}}} \right)$$

$$K_{a3} = 7.5 \times 10^{-3}, \quad \therefore K_{a3}^2 = 56.25 \times 10^{-6}$$

$$\text{For a } 0.02(M) \text{ } H_3PO_4 \text{ solution } (C = 0.02 \text{ mol.lit}^{-1}), \quad \sqrt{K_{a3}^2 + 4CK_{a3}} = 0.0256$$

$$\therefore [H^+] = \frac{0.018}{2} (M)$$

$$\therefore p[H^+] = 2.046 \approx 2.05$$

Similarly, it may be shown that $p[H]$ of a 1 (M) solution of H_3PO_4 will be equal to 1.08.

Assuming $C \gg [H^+]$, so that $C - [H^+] \approx C$, $p[H]$ of H_3PO_4 solution may be calculated using the relation,

$$K_{a3} = \frac{[H^+]^2}{C}$$

$$\therefore p[H] = \frac{1}{2} pK_{a3} - \frac{1}{2} \log C$$

$$\text{Since, } K_{a3} = 7.5 \times 10^{-3}, \quad \therefore pK_{a3} = 2.12$$

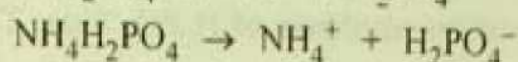
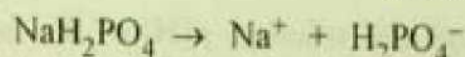
Thus, $p[H]$ of 0.02 (M) H_3PO_4 solution will be,

$$p[H] = \frac{1}{2} (2.12) - \frac{1}{2} \log(0.02) = 1.91$$

and $p[H]$ of 1 (M) H_3PO_4 solution becomes equal to 1.06, which are slightly lower than the actual values.

(ii) $p[H]$ of a mixture of H_3PO_4 and its primary salt, NaH_2PO_4 or $NH_4H_2PO_4$

In aqueous solution, the salt NaH_2PO_4 or $NH_4H_2PO_4$ ionizes completely, producing equimolar amount of $H_2PO_4^-$ ion, which depresses the ionization of H_3PO_4 appreciably by common ion effect:



Ionization of water ($K_w = 10^{-14}$) is negligible in comparison to that of H_3PO_4 . The mixture of conjugate acid - base pair, H_3PO_4 and H_2PO_4^- constitutes a buffer solution, of which the $p[\text{H}]$ is given by *Handerson-Hasselbalch* equation,

$$p[\text{H}] = pK_{a3} + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$

If the mixture contains equimolar concentrations of H_3PO_4 and NaH_2PO_4 , i.e., $[\text{H}_3\text{PO}_4] = [\text{H}_2\text{PO}_4^-]$, then $p[\text{H}]$ of this buffer solution becomes equal to pK_{a3} of H_3PO_4 (2.12), since, in presence of the completely ionized salt, ionization of H_3PO_4 remains sufficiently depressed, so that the equilibrium concentration of $[\text{H}_3\text{PO}_4]$ is equal to its analytical concentration.

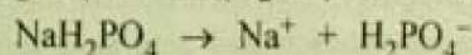
Examples (2.10)

- (i) Find the $p[\text{H}]$ of a solution which is 0.2 M in H_3PO_4 and 0.4M in NaH_2PO_4 . [Given: pK_{a3} of $\text{H}_3\text{PO}_4 = 2.12$].

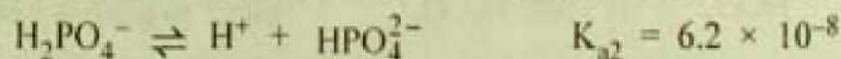
$$\begin{aligned} p[\text{H}] &= pK_{a3} + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\ &= pK_{a3} + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \\ &= 2.12 + \log \left(\frac{0.4}{0.2} \right) \\ &= 2.12 + \log 2 = 2.421 \approx 2.42 \end{aligned}$$

- (ii) $p[\text{H}]$ at the first equivalence point of H_3PO_4 , i.e., $p[\text{H}]$ of an aqueous solution of NaH_2PO_4 or $\text{NH}_4\text{H}_2\text{PO}_4$.

The salt, NaH_2PO_4 (or $\text{NH}_4\text{H}_2\text{PO}_4$) is completely ionized in aqueous solution.



Neither Na^+ ion nor NH_4^+ shows any acidic or basic property. The anion, H_2PO_4^- may undergo both protonation and deprotonation in aqueous solution:



Net reaction:



$$\therefore [\text{H}_3\text{PO}_4] = [\text{HPO}_4^{2-}]$$

Both K_{a3} and K_{a2} are much larger than $K_w = (10^{-14})$. So, ionization equilibrium of water

can not influence the H^+ ion concentration of this solution. $p[H]$ of this solution is governed only by the above protonation- deprotonation equilibria of $H_2PO_4^-$ ion. Thus,

$$K_{a3} \cdot K_{a2} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \times \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} = [H^+]^2$$

$$\therefore \frac{1}{[H^+]} = K_{a3}^{-1/2} \cdot K_{a2}^{-1/2}$$

$$\therefore p[H] = \frac{1}{2} pK_{a3} + \frac{1}{2} pK_{a2}$$

Thus, $p[H]$ of aqueous solution of an acid-salt of a polybasic acid is independent of concentration of the acid-salt.

$p[H]$ of an aqueous solution of ammonium dihydrogenphosphate, $(NH_4)H_2PO_4$ will also be given by the above equation, since, NH_4^+ ion, will not show any acid reaction in presence of H_3PO_4 and $H_2PO_4^-$ which are much stronger acids than NH_4^+ ($pK_{NH_4^+} = 9.26$).

Examples (2.11)

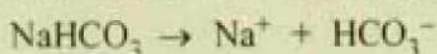
- (1) Calculate the $p[H]$ of an aqueous solution of sodium dihydrogenphosphate (NaH_2PO_4).

[Given: for H_3PO_4 : $pK_{a1} = 12.32$, $pK_{a2} = 7.21$, $pK_{a3} = 2.12$]

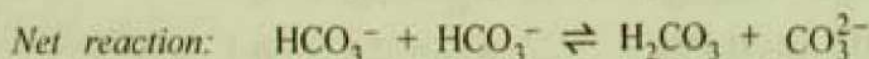
$$\begin{aligned} p[H] &= \frac{1}{2} pK_{a3} + \frac{1}{2} pK_{a2} \\ &= \frac{1}{2} (2.12 + 7.21) = 4.665 \approx 4.67 \end{aligned}$$

- (2) What will be the $p[H]$ of a of 0.2(M) aqueous solution of sodium bicarbonate? [Given: for carbonic acid $pK_{a2} = 6.37$ $pK_{a1} = 10.25$].

The acid-salt, sodium bicarbonate, $NaHCO_3$, is completely ionized in aqueous solution,



Na^+ ion shows neither acidic nor basic property. The bicarbonate ion, HCO_3^- , undergoes protonation-deprotonation equilibria in aqueous solution and acts as a *self-buffer*:



$$\therefore [H_2CO_3] = [CO_3^{2-}]$$

pK_w of water is 14, which indicates ionization of water is almost negligible in comparison to deprotonation of HCO_3^- ($pK_{a1} = 10.25$). Therefore, $p[H]$ of this solution will be governed only by the protonation-deprotonation equilibria of HCO_3^- ion.

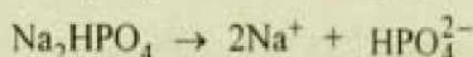
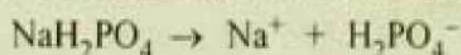
$$\therefore K_{H_2CO_3} \cdot K_{HCO_3} = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \times \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = [H^+]^2$$

$$\begin{aligned}\therefore p[H] &= \frac{1}{2}(pK_{H_2CO_3} + pK_{HCO_3}) \\ &= \frac{1}{2}(6.37 + 10.25) = 8.31\end{aligned}$$

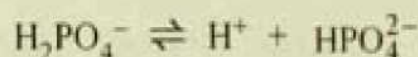
Note that the $p[H]$ of the solution is independent of concentration of $NaHCO_3$.

(iv) $p[H]$ of an aqueous solution of a mixture of NaH_2PO_4 and Na_2HPO_4

Both the salts are completely ionized in aqueous solution:



Na^+ ion shows no acid-base property. The two anions, $H_2PO_4^-$ and HPO_4^{2-} , constitute a conjugate acid-base pair:



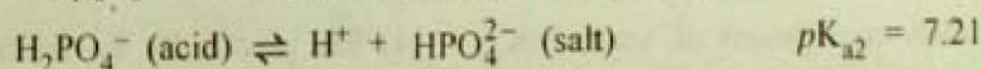
So, the mixture of these two salts will form a buffer solution, in which $H_2PO_4^-$ ($pK_{a2} = 7.21$ at $25^\circ C$) will serve as a weak acid and HPO_4^{2-} will serve as its salt (or conjugate base). Since the deprotonation constant of HPO_4^{2-} ($K_{a1} = 4.8 \times 10^{-13}$ at $25^\circ C$) and the ionic product of water ($K_w = 10^{-14}$ at $25^\circ C$) are much lower than the deprotonation constant of $H_2PO_4^-$ ($K_{a2} = 6.8 \times 10^{-8}$ at $25^\circ C$), only the deprotonation equilibrium of $H_2PO_4^-$ ion will be operative. Consequently, $p[H]$ of this mixture will be given by *Handerson-Hasselbalch equation*,

$$p[H] = pK_{a2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

Examples (2.12)

- (1) Calculate the $p[H]$ of a solution which is $0.25M$ in NaH_2PO_4 and $0.50M$ in Na_2HPO_4 . [Given: for H_3PO_4 : $pK_{a1} = 12.32$, $pK_{a2} = 7.21$ and $pK_{a3} = 2.12$ at $25^\circ C$]

The mixture of NaH_2PO_4 and Na_2HPO_4 constitutes a conjugate acid-base pair, forming a buffer solution, $p[H]$ of which will be governed by the equilibrium:



$$\therefore p[H] = pK_{a2} + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

$$= 7.21 + \log \left(\frac{0.50}{0.25} \right) = 7.21 + \log 2 = 7.511.$$

- (2) In what molar proportion should NaH_2PO_4 and Na_2HPO_4 be mixed so as to obtain a buffer solution of $p[\text{H}] = 7$? [Given: for H_3PO_4 , $pK_{a3} = 2.12$, $pK_{a2} = 7.21$ and $pK_{a1} = 12.32$ at 25°C].

The equilibrium responsible for the buffering action of the mixture of NaH_2PO_4 and Na_2HPO_4 is the deprotonation equilibrium of H_2PO_4^- ion,



$p[\text{H}]$ of this buffer solution will be given by the equation,

$$p[\text{H}] = pK_{a2} + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$\therefore \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \text{Inverse log } (p[\text{H}] - pK_{a2})$$

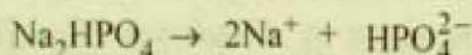
For a buffer solution of $p[\text{H}] = 7$,

$$\frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = \text{Inverse log}(7 - 7.21) = 0.617 \approx 0.62$$

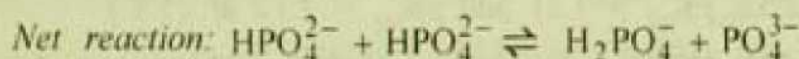
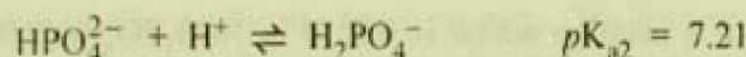
$$\therefore [\text{NaH}_2\text{PO}_4] : [\text{Na}_2\text{HPO}_4] = 1 : 0.62$$

- (v) $p[\text{H}]$ of an aqueous solution of Na_2HPO_4

The salt ionizes completely in aqueous solution according to,



Na^+ ion shows no acid-base property. HPO_4^{2-} ion in aqueous solution undergoes both deprotonation as well as protonation equilibria:



$$(\therefore [\text{H}_2\text{PO}_4^-] = [\text{PO}_4^{3-}])$$

Ionization equilibrium of water ($pK_w = 14$) has practically no contribution to H^+ ion concentration of this solution, $p[\text{H}]$ of which is totally governed by the protonation-deprotonation equilibria of HPO_4^{2-} ion. Thus,

$$K_{a1} \cdot K_{a2} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \times \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = [\text{H}^+]^2$$

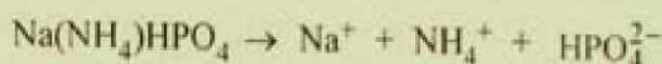
$$\therefore p[H] = \frac{1}{2}(pK_{a1} + pK_{a2})$$

$$= \frac{1}{2}(12.32 + 7.21) = 9.765 \approx 9.77$$

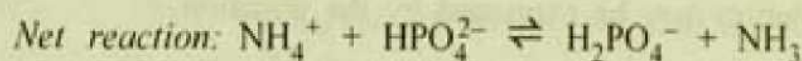
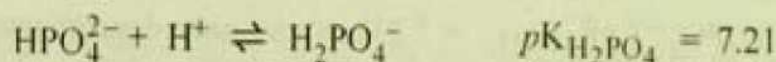
So, $p[H]$ of Na_2HPO_4 solution is independent of concentration of this salt.

(vi) $p[H]$ of an aqueous solution of $\text{Na}(\text{NH}_4)\text{HPO}_4$

Like Na_2HPO_4 , this salt produces HPO_4^{2-} ion by complete ionization in aqueous solution.



Although Na^+ ion is neutral, but NH_4^+ ion ($pK_{\text{NH}_4} = 9.26$) shows acidic property. On the other hand, HPO_4^{2-} ion ($pK_{\text{HPO}_4} = 12.32$) appears to be a much weaker acid in comparison to NH_4^+ ion. It can not undergo deprotonation in presence of NH_4^+ ion, but, it can show its basic property, by accepting the proton released by NH_4^+ ion, since $pK_{\text{H}_2\text{PO}_4} = 7.21$.



$$\therefore [\text{H}_2\text{PO}_4^-] = [\text{NH}_3]$$

and $[\text{NH}_4^+] = [\text{HPO}_4^{2-}]$

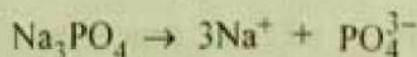
$$\therefore K_{\text{NH}_4} \cdot K_{\text{H}_2\text{PO}_4} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} \times \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = [\text{H}^+]^2$$

$$\therefore p[H] = \frac{1}{2}(pK_{\text{NH}_4} + pK_{\text{H}_2\text{PO}_4})$$

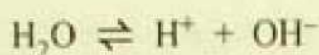
$$= \frac{1}{2}(9.26 + 7.21) = 8.235 \approx 8.24$$

(vii) $p[H]$ of an aqueous solution of sodium phosphate (Na_3PO_4)

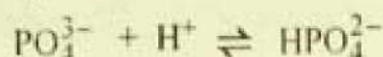
The salt ionizes completely in aqueous solution according to,



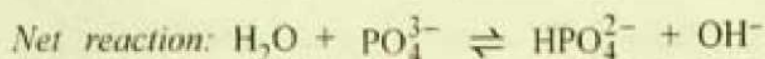
Na^+ ion shows neither acidic nor basic property. PO_4^{3-} ion is the conjugate base of HPO_4^{2-} ion, which is a very weak acid ($pK_{\text{HPO}_4} = 12.32$). So, PO_4^{3-} ion is a very strong base and it will tend to take up protons from H_2O molecules of liquid water. That is, ionization equilibrium of H_2O molecule is also operative in the presence of strongly basic PO_4^{3-} ion. The dominating protonation-deprotonation equilibria in this solution are,



$$pK_w = 14 \text{ (at } 25^\circ\text{C)}$$



$$pK_{\text{HPO}_4} = 12.32 \text{ (at } 25^\circ\text{C)}$$



$$\therefore [\text{HPO}_4^{2-}] = [\text{OH}^-]$$

$$K_w \cdot K_{\text{HPO}_4} = [\text{H}^+][\text{OH}^-] \times \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} = [\text{H}^+]^2[\text{PO}_4^{3-}]$$

$$\therefore \frac{1}{[\text{H}^+]} = \left(\frac{[\text{PO}_4^{3-}]}{K_w \cdot K_{\text{HPO}_4}} \right)^{\frac{1}{2}}$$

$$\therefore p[\text{H}] = \frac{1}{2} pK_w + \frac{1}{2} pK_{\text{HPO}_4} + \frac{1}{2} \log[\text{PO}_4^{3-}]$$

If the concentration of the salt, Na_3PO_4 , is $C \text{ mol. lit}^{-1}$, then the equilibrium concentration of PO_4^{3-} ion may also be taken as $C \text{ mol. lit}^{-1}$, without any serious error, since HPO_4^{2-} ion, that is produced due to protonation of PO_4^{3-} ion, can not take up further protons from water ($pK_w = 14$) to produce H_2PO_4^- ($pK_{\text{H}_2\text{PO}_4} = 7.21$), it can only deprotonate back to produce PO_4^{3-} ion, therefore, $p[\text{H}]$ of the solution may be expressed by the equation,

$$p[\text{H}] = \frac{1}{2} pK_w + \frac{1}{2} pK_{\text{HPO}_4} + \frac{1}{2} \log C$$

Example (2.13)

Calculate the $p[\text{H}]$ of 0.2 (M) solution of sodium phosphate in water [Given: $pK_w = 14$, $pK_{\text{HPO}_4} = 12.32$ at 25°C].

$$\begin{aligned} p[\text{H}] &= \frac{1}{2} pK_w + pK_{\text{HPO}_4} + \frac{1}{2} \log C \\ &= \frac{1}{2} (14) + \frac{1}{2} (12.32) + \frac{1}{2} \log(0.2) \\ &= 7 + 6.16 - 0.35 = 12.81 \end{aligned}$$

(f) Aqueous Solutions of Salts

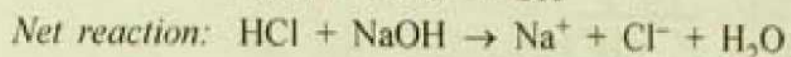
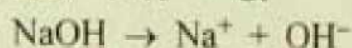
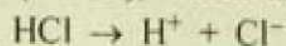
Salt solutions in water may be neutral, acidic or alkaline, depending upon the acid-base properties of the constituent cations and anions, i.e., the strengths of the constituent acid and the base, forming the salt. As a general rule, aqueous solutions of salts of strong acids with strong bases (eg. NaCl) are neutral, salt of a strong acid with a weak base (eg. NH_4Cl) gives acidic reaction and salt of a weak acid with a strong base (eg. CH_3COONa) gives alkaline reaction in aqueous solution. Thus, the influence of the stronger partner dominates the acid-base property of the aqueous solutions of salts, as summarized below:



- (i) Strong acid + strong base $\rightarrow$ Salt $\rightarrow$ Aq. solution $\rightarrow$ Neutral
- (ii) Strong acid + weak base $\rightarrow$ Salt $\rightarrow$ Aq. solution $\rightarrow$ Acidic
- (iii) Weak acid + strong base $\rightarrow$ Salt $\rightarrow$ Aq. solution $\rightarrow$ Alkaline

(i) Salts yielding neutral solutions in water

Salt of strong acid with a strong base, such as sodium chloride (NaCl) dissolves in water giving neutral solution. It is derived from hydrochloric acid (HCl), which is a strong acid and sodium hydroxide (NaOH), which is a strong base:



Since HCl is a strong acid in water, it ionizes completely to produce H^+ ion and its conjugate base Cl^- ion, is a weak base, having practically no tendency to pick up a proton from water to make the solution alkaline. Similarly, NaOH is a strong base, it ionizes completely in aqueous solution to produce Na^+ ion and OH^- ion, which is the actual base. Since OH^- ion is a strong base, its conjugate acid, Na^+ ion, more appropriately the hydrated $\text{Na}(\text{aq})^+$ ion, $[\text{Na}(\text{H}_2\text{O})_6]^+$, is a weak acid, having negligible tendency to make the solution acidic by releasing a proton to the solution.

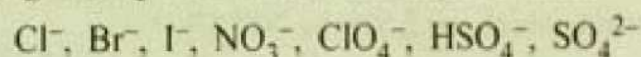
In general, alkali and alkaline earth metal ions and anions of strong monoprotic acids eg. HCl, HBr, HI, HNO_3 , HClO_4 etc. respectively show no tendency to react with water to produce either H^+ or OH^- ion. So the corresponding salt solutions are neutral.

Cations of strong bases:

Alkali metal cations of periodic Group-1 : Li^+ , Na^+ , K^+

Alkaline earth metal ions of periodic Group 2 : Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , (except Be^{2+})

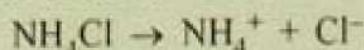
Anions of strong monoprotic acids and sulfuric acid:



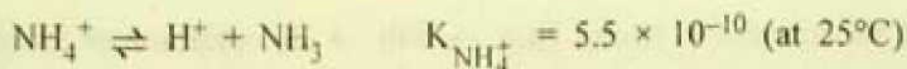
Aqueous solutions of salts containing these cations and anions are neutral ($p[\text{H}] \approx 7$), but due to absorption of atmospheric CO_2 , these solutions show slightly acidic property, ($p[\text{H}] \leq 7$) (since, $pK_{\text{H}_2\text{CO}_3} = 6.37$).

(ii) Salts yielding acidic solutions in water

Salts such as NH_4Cl , derived from strong acid (HCl) and weak base (NH_3) give acidic reaction in aqueous solution. These salts ionize in aqueous solution completely,



Since Cl^- ion is the conjugate base of the strong acid (HCl), it is a weak base having practically no tendency to bind with proton from water. NH_4^+ ion, on the other hand, is the conjugate acid of the weak base (NH_3), so it has a profound tendency to give up protons to aqueous solution, making it weakly acidic.



$$\therefore [\text{H}^+] = [\text{NH}_3]$$

Ionization of H_2O molecules of solvent water has negligible contribution to the acidity of this solution, since, $K_w = 10^{-14}$ (at 25°C), which is $\sim 10^4$ times smaller than $K_{\text{NH}_4^+}$. So, $p[\text{H}]$ of this solution will be governed by the concentration of NH_4^+ ion only. If $C \text{ mol. lit}^{-1}$, be the analytical concentration of the salt, NH_4Cl , then equilibrium concentration of NH_4^+ ion is $[\text{NH}_4^+] = C - [\text{H}^+]$. Therefore,

$$K_{\text{NH}_4^+} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{[\text{H}^+]^2}{C - [\text{H}^+]}$$

Since, NH_4^+ ion is a weak acid, the equilibrium concentration of H^+ ion will be negligibly small in comparison to the analytical concentration of NH_4Cl , that is,

$$[\text{NH}_4^+] = C - [\text{H}^+] \approx C$$

$$\therefore K_{\text{NH}_4^+} = \frac{[\text{H}^+]^2}{C}$$

$$\therefore \frac{1}{[\text{H}^+]} = \left[\frac{1}{(K_{\text{NH}_4^+} \cdot C)} \right]^{\frac{1}{2}}$$

$$\therefore p[\text{H}] = \frac{1}{2} pK_{\text{NH}_4^+} - \frac{1}{2} \log C$$

Examples (2.14)

(1) Calculate the $p[\text{H}]$ of a solution which is 2.5% in NH_4Cl .

$$[\text{Given: } K_{\text{NH}_4^+} = 5.5 \times 10^{-10} \text{ at } 25^\circ\text{C}]$$

$$\therefore K_{\text{NH}_4^+} = 5.5 \times 10^{-10}$$

$$\therefore pK_{\text{NH}_4^+} = 9.26$$

$$\text{Formula weight of } \text{NH}_4\text{Cl} = 14 + (1 \times 4) + 35.5 = 53.5$$

100 ml of NH_4Cl solution contains 2.5g NH_4Cl .

$\therefore$ 1000 ml of NH_4Cl solution contains 25 g NH_4Cl .

$$\therefore \text{Strength of } \text{NH}_4\text{Cl} \text{ solution} = \left(\frac{25}{53.5} \right) M = 0.467 M$$

$$\therefore [\text{NH}_4^+] = 0.467 M$$

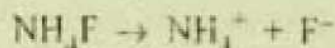
$$p[H] = \frac{1}{2} pK_{NH_4^+} - \frac{1}{2} \log[NH_4^+]$$

$$= \frac{1}{2} (9.26) - \frac{1}{2} \log(0.467) = 4.795 = 4.8$$

(2) What will be the $p[H]$ of a 0.2 M solution of ammonium fluoride?

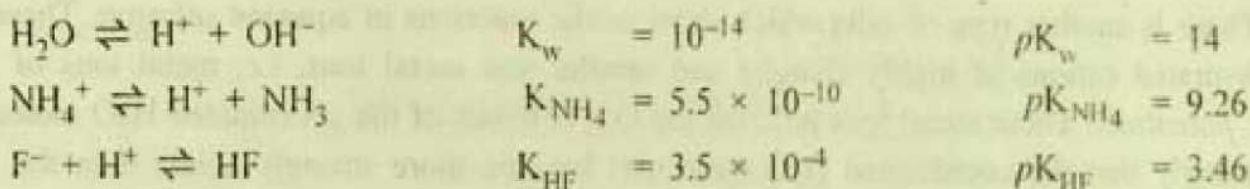
[Given : $K_{HF} = 3.5 \times 10^{-4}$, $K_{NH_4} = 5.5 \times 10^{-10}$, $K_w = 10^{-14}$ at $25^\circ C$]

NH_4F ionizes completely in aqueous solution,



$$\therefore [NH_4^+] = [F^-] = [NH_4F]$$

Now F^- ion is the conjugate base of a weak acid (HF), so it has a tendency to bind with protons of H_2O . NH_4^+ ion is the conjugate acid of a weak base (NH_3), so it has a tendency to give up protons. The possible protonation-deprotonation equilibria in aqueous solution are,



As the magnitudes of the ionization constants imply, ionization equilibrium of water has negligible contribution to the H^+ ion concentration of this solution. Thus, the net acid-base equilibrium in solution is,



$$\therefore [HF] = [NH_3]$$

$$\therefore K_{NH_4} \cdot K_{HF} = \frac{[H^+][NH_3]}{[NH_4^+]} \times \frac{[H^+][F^-]}{[HF]} = [H^+]^2$$

$$\therefore \frac{1}{[H^+]} = \left(\frac{1}{K_{NH_4}} \cdot \frac{1}{K_{HF}} \right)^{\frac{1}{2}}$$

$$\therefore p[H] = \frac{1}{2} (pK_{NH_4} + pK_{HF})$$

$$= \frac{1}{2} (9.26 + 3.46) = 6.36$$

(3) Calculate the $p[H]$ of an aqueous solution of 0.25 M ammonium bifluoride. [Given: $pK_{HF} = 3.46$, $pK_{NH_4} = 9.26$].

NH_4HF_2 may be regarded as a 1:1 mixture of NH_4F and HF, i.e., a mixture of weak acid (HF) and one of its salt (NH_4F). So an aqueous solution of NH_4HF_2 will constitute

a buffer solution in which the molar ratio of the [salt] : [acid] is 1:1. Therefore, $p[H]$ of this solution will be equal to the pK_a of the acid (i.e., pK_{HF}):

$$\begin{aligned} p[H] &= pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= pK_{HF} + \log \frac{[NH_4F]}{[HF]} \\ &= pK_{HF} = 3.46 \quad (\because [NH_4F] = [HF]). \end{aligned}$$

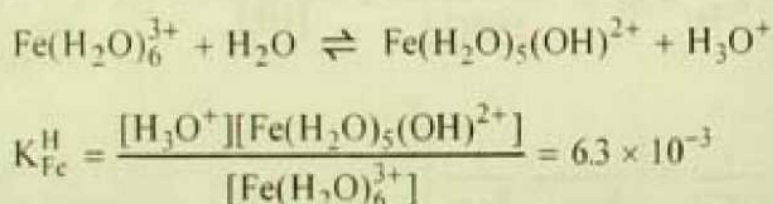
Since, $pK_{HF} \ll pK_{NH_4}$, NH_4^+ ion can not show its acidic reaction in presence of HF. Thus, $p[H]$ of NH_4HF_2 solution will be independent of its concentration.

Note: $p[H]$ of an aqueous solution KHF_2 will similarly be independent of its concentration and will be equal to pK_{HF} , since the salt may be regarded as a 1:1 mixture of KF and HF.

(iii) $p[H]$ of aqueous solutions of hydrated metal ions

There is another type of salts which show acidic reactions in aqueous solution. These are the hydrated cations of highly charged and smaller size metal ions, i.e., metal ions of high ionic potentials. These metal ions polarize the O – H bonds of the coordinated H_2O molecules so strongly that the coordinated H_2O molecules become more strongly acidic than the H_2O molecules in the solvent water. Among the representative metal ion, Be^{2+} and Al^{3+} ions are significantly acidic. Most transition metal ions, particularly in their higher oxidation states, eg, Fe^{III} , Co^{III} , Cr^{III} , Ti^{IV} , Zr^{IV} etc. show significantly acidic behaviour. Some metal ions readily form *oxyanions*, e.g., Bi^{III} , Zr^{IV} , etc. Acidity of hydrated representative metal ions fall in the order : $Al^{3+} \gg Mg^{2+} > Na^+$; $Be^{2+} \gg Li^+$.

Deprotonation equilibrium of a hydrated metal ion may be represented with $Fe(H_2O)_6^{3+}$ ion as an example,



These deprotonation reactions may also be termed as *hydrolysis* reactions of the aqua metal ions. K_M^H values of some common metal ions are given in Table 2.2.

Table 2.2. Deprotonation constants (K_M^H) of some hydrated metallic cations at 25°C.

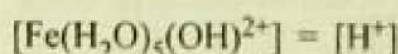
$M^{n+}(aq)$	K_M^H	$M^{n+}(aq)$	K_M^H
$Fe^{3+}(aq)$	6.3×10^{-3}	$Co^{2+}(aq)$	1.3×10^{-9}
$Cr^{3+}(aq)$	1.6×10^{-4}	$Zn^{2+}(aq)$	2.5×10^{-10}
$Al^{3+}(aq)$	1.4×10^{-5}	$Fe^{2+}(aq)$	3.2×10^{-10}
$Be^{2+}(aq)$	3×10^{-7}	$Ni^{2+}(aq)$	2.5×10^{-11}

Thus, $\text{Fe}^{3+}(\text{aq})$, $\text{Al}^{3+}(\text{aq})$, $\text{Cr}^{3+}(\text{aq})$ ions are stronger acids in aqueous solution than acetic acid (1.8×10^{-5}). Acidity of the hydrated transition metal ions listed above fall in the order:

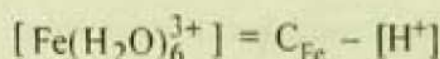


$p[\text{H}]$ of aqueous solutions of salts of these metal ions with strong acids will depend upon the concentration of the hydrated salt cations and their deprotonation constants (K_M^H values), just in the same manner as the aqueous solutions of weak acids.

For the first step deprotonation of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ion presented above, at equilibrium,



If C_{Fe} be the analytical concentration of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ion, then the equilibrium concentration of $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ion will be,



Therefore,

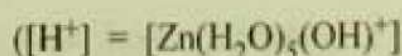
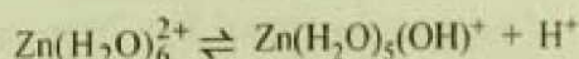
$$K_{\text{Fe}}^H = \frac{[\text{H}^+][\text{Fe}(\text{H}_2\text{O})_5(\text{OH})^{2+}]}{[\text{Fe}(\text{H}_2\text{O})_6^{3+}]} = \frac{[\text{H}^+]^2}{C_{\text{Fe}} - [\text{H}^+]}$$

$$\therefore [\text{H}^+]^2 + K_{\text{Fe}}^H[\text{H}^+] - C_{\text{Fe}}K_{\text{Fe}}^H = 0$$

Neglecting the negative root,

$$[\text{H}^+](+) = \frac{-K_{\text{Fe}}^H + \sqrt{(K_{\text{Fe}}^H)^2 + 4C_{\text{Fe}}K_{\text{Fe}}^H}}{2}$$

Substituting the values of K_{Fe}^H and C_{Fe} , one may calculate $[\text{H}^+]$ and from there, $p[\text{H}]$ of the aqueous solution of the salt. This rigorous calculation is required when the hydrated metallic ion is moderately strongly acidic, e.g. $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{H}_2\text{O})_6^{3+}$, $\text{Ti}(\text{H}_2\text{O})_6^{4+}$ etc. But when the hydrated metal ion is weakly acidic, eg. $\text{Zn}(\text{H}_2\text{O})_6^{2+}$, $\text{Ni}(\text{H}_2\text{O})_6^{2+}$, etc., concentration of H^+ ion produced by deprotonation of coordinated H_2O molecules of the hydrated metal ion is negligibly small in comparison to the analytical concentration of the hydrated metal ion. As for example, for hydrated $\text{Zn}(\text{H}_2\text{O})_6^{2+}$ ion,



$$K_{\text{Zn}}^H = \frac{[\text{H}^+][\text{Zn}(\text{H}_2\text{O})_5(\text{OH})^+]}{[\text{Zn}(\text{H}_2\text{O})_6^{2+}]} = 2.5 \times 10^{-10} \text{ (at } 25^\circ\text{C)}$$

If C_{Zn} = analytical concentration of $Zn(H_2O)_6^{2+}$ ion, then the equilibrium concentration of $Zn(H_2O)_6^{2+}$ will be,

$$[Zn(H_2O)_6^{2+}] = C_{Zn} - [H^+] \approx C_{Zn} \quad (\because K_{Zn}^H = 2.5 \times 10^{-10})$$

Ionization equilibrium of H_2O does not influence the $p[H]$ of these solutions, since $K_w = 10^{-14}$ is much lower than the K_M^H values.

$$\therefore K_{Zn}^H = \frac{[H^+].[H^+]}{C_{Zn} - [H^+]} \approx \frac{[H^+]^2}{C_{Zn}}$$

$$\therefore \frac{1}{[H^+]} = \left(\frac{1}{K_{Zn}^H} \cdot \frac{1}{C_{Zn}} \right)^{\frac{1}{2}}$$

$$\therefore p[H] = \frac{1}{2} pK_{Zn}^H - \frac{1}{2} \log C_{Zn}$$

Examples (2.15)

- (1) Calculate the $p[H]$ of an aqueous solution of 0.002 M zinc sulfate. [Given: $K_{Zn}^H = 2.5 \times 10^{-10}$ at $25^\circ C$].

$$pK_{Zn}^H = -\log K_{Zn}^H = -\log 2.5 \times 10^{-10} = 9.60$$

$$\begin{aligned} p[H] &= \frac{1}{2} pK_{Zn}^H - \frac{1}{2} \log C_{Zn} \\ &= \frac{1}{2} (9.6) - \frac{1}{2} \log(0.002) = 6.15 \end{aligned}$$

- (2) Calculate the $p[H]$ of 0.001 M solution of aluminium nitrate. [Given: $K_{Al}^H = 1.4 \times 10^{-5}$ at $25^\circ C$]

$$pK_{Al}^H = -\log K_{Al}^H = -\log(1.4 \times 10^{-5}) = 4.85$$

$$\begin{aligned} p[H] &= \frac{1}{2} pK_{Al}^H - \frac{1}{2} \log C_{Al} \\ &= \frac{1}{2} (4.85) - \frac{1}{2} \log(0.001) = 3.925 \approx 3.93 \end{aligned}$$

Since $Al(H_2O)_6^{3+}$ ion appears to be a moderately weak acid, equilibrium concentration of $Al(H_2O)_6^{3+}$ ion may be taken as $[Al(H_2O)_6^{3+}] = C_{Al} - [H^+]$. Using the expression for K_{Al}^H and assuming $[H^+] = [Al(H_2O)_5(OH)^{2+}]$, one obtains,

$$[H^+]^2 + K_{Al}^H[H^+] - C_{Al} \cdot K_{Al}^H = 0$$

$$C_{Al} = 0.001 \text{ (M)}$$

$$K_{Al}^H = 1.4 \times 10^{-5}$$

Neglecting the negative root, one obtains,

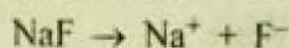
$$\begin{aligned} [H^+]_{(+)} &= \frac{-K_{Al}^H + \sqrt{(K_{Al}^H)^2 + 4C_{Al} \cdot K_{Al}^H}}{2} \\ &= \frac{-(1.4 \times 10^{-5}) + \sqrt{(1.4 \times 10^{-5})^2 + 4 \cdot (0.001) \cdot (1.4 \times 10^{-5})}}{2} = 1.115 \times 10^{-4} \end{aligned}$$

$$\therefore p[H] = 3.95$$

So, the two methods of calculation give almost the same result.

(iv) Salts yielding alkaline solutions

Salts of weak acids with strong bases belong to this category. Salts of weak acids such as HF, HCN, HNO₂, CH₃COOH, H₂CO₃ with strong bases such as NaOH or KOH give alkaline reaction in aqueous solution. The salts ionize completely in aqueous solution, eg.

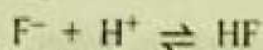


$$\therefore [\text{F}^-] = [\text{NaF}]$$

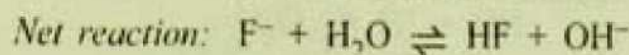
The salt cation (Na⁺) shows neither acidic nor basic property. But the salt anion F⁻, being the conjugate base of a weak acid (HF, K_{HF} = 3.5 × 10⁻⁴ at 25°C), is a moderately strong base and may take up a proton released from ionization of water, setting free OH⁻ ion in aqueous solution, rendering it alkaline.



$$K_w = 10^{-14} \text{ (at } 25^\circ \text{ C)}$$



$$K_{HF} = 3.5 \times 10^{-4} \text{ (at } 25^\circ \text{ C)}$$



$$\therefore [\text{HF}] = [\text{OH}^-]$$

This net reaction may also be termed as *hydrolysis* of F⁻ ion. Thus,

$$K_{HF} \cdot K_w = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} \times [\text{H}^+][\text{OH}^-] = [\text{H}^+]^2[\text{F}^-]$$

$$\therefore \frac{1}{[\text{H}^+]} = \left(\frac{[\text{F}^-]}{K_{HF} \cdot K_w} \right)^{\frac{1}{2}}$$

$$\therefore p[H] = \frac{1}{2} pK_w + \frac{1}{2} pK_{HF} + \frac{1}{2} \log[F^-]$$

If the concentration of NaF is $C \text{ mol.lit}^{-1}$, then the equilibrium concentration of F⁻ ion will be,

$[F^-] = C - [HF] = C - [OH^-] \approx C$, since OH^- is produced by ionization of H_2O , for which $K_w = 10^{-14}$ is very small compared to K_{HF} .

$$\therefore p[H] = \frac{1}{2} pK_w + \frac{1}{2} pK_{HF} + \frac{1}{2} \log C.$$

Examples (2.16)

- (1) Calculate the $p[H]$ of 0.2 M solution of NaF in water. [Given: $K_{HF} = 3.5 \times 10^{-4}$, $K_w = 10^{-14}$ at $25^\circ C$]

$$C = 0.2 \text{ (M)}$$

$$pK_{HF} = -\log K_{HF} = -\log(3.5 \times 10^{-4}) = 3.46$$

$$pK_w = -\log K_w = -\log(10^{-14}) = 14$$

$$\therefore p[H] = \frac{1}{2} pK_w + \frac{1}{2} pK_{HF} + \frac{1}{2} \log C$$

$$= \frac{1}{2} (14) + \frac{1}{2} (3.46) + \frac{1}{2} \log(0.2) = 8.38$$

- (2) Calculate the $p[H]$ of 0.1 M solution of KCN in water.

[Given: $K_{HCN} = 4.9 \times 10^{-10}$, $K_w = 10^{-14}$ at $25^\circ C$].

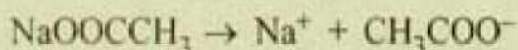
$$pK_{HCN} = -\log(4.9 \times 10^{-10}) = 9.31, pK_w = -\log 10^{-14} = 14, C = 0.1 \text{ M}$$

$$\therefore p[H] = \frac{1}{2} pK_w + \frac{1}{2} pK_{HCN} + \frac{1}{2} \log C$$

$$= \frac{1}{2} (14 + 9.31) + \frac{1}{2} \log(0.1) = 11.16$$

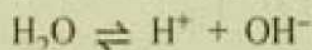
- (3) Calculate the $p[H]$ of 0.20 M solution of sodium acetate in water.

(Given: $K_a = 1.8 \times 10^{-5}$ at $25^\circ C$).

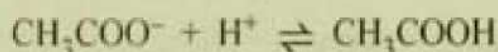


$$\therefore [CH_3COO^-] = [NaOOCCH_3] = 0.2 \text{ M} = C$$

The protonation-deprotonation equilibria involved are,



$$pK_w = 10^{-14}$$



$$K_a = 1.8 \times 10^{-5}, pK_a = 4.74$$

Net reaction: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

$$\therefore [CH_3COOH] = [OH^-]$$

$$\therefore K_w K_a = [H^+][OH^-] \times \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = [H^+]^2 [CH_3COO^-]$$

$$\therefore K_w K_a = [H^+]^2 C$$

$$\therefore \frac{1}{[H^+]} = \left(\frac{C}{K_w K_a} \right)^{\frac{1}{2}}$$

$$\therefore p[H] = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log C$$

$$= \frac{1}{2} (14) + \frac{1}{2} (4.74) + \frac{1}{2} \log(0.2) = 9.02$$

- (4) Calculate the $p[H]$ of a 2% solution of anhydrous sodium carbonate in water. [Given: for carbonic acid, $K_{a2} = 4.3 \times 10^{-7}$, $K_{a1} = 5.6 \times 10^{-11}$]

Formula weight of anhydrous $Na_2CO_3 = (23 \times 2) + 12 + (16 \times 3) = 106$

$\therefore 106 \text{ g of anhydrous } Na_2CO_3 \text{ in } 1000 \text{ ml} \equiv 1 \text{ M } Na_2CO_3$

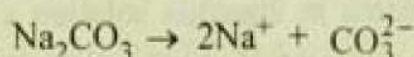
$\therefore 10.6 \text{ g of anhydrous } Na_2CO_3 \text{ } 100 \text{ ml} \equiv 1 \text{ M } Na_2CO_3$

$\therefore 10.6\% \text{ } Na_2CO_3 \text{ solution} \equiv 1 \text{ M } Na_2CO_3 \text{ solution}$

$\therefore 2\% \text{ } Na_2CO_3 \text{ solution} = \left(\frac{2}{10.6} \right) \text{ M } Na_2CO_3 \text{ solution}$

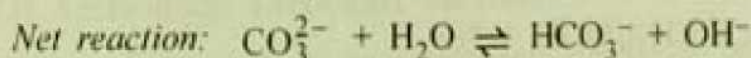
$= 0.189 \text{ M } Na_2CO_3 \text{ solution.}$

Na_2CO_3 is completely ionized in aqueous solution.



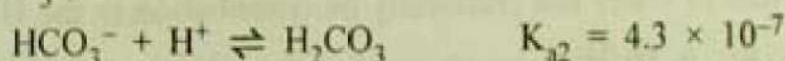
$$\therefore [CO_3^{2-}] = [Na_2CO_3] = 0.189 \text{ M} = C$$

As H_2CO_3 is a weak acid, HCO_3^- is much weaker, so its conjugate base, CO_3^{2-} ion is a strong base and has a strong tendency to be protonated by the H^+ ion released from ionization of H_2O molecules,



$$\therefore [HCO_3^-] = [OH^-]$$

Since $K_{a2} (= 4.3 \times 10^{-7})$ of H_2CO_3 is much higher than K_{a1} and K_w values, the protonation equilibrium of HCO_3^- ,



remains totally left shifted. Therefore, only the ionization equilibrium of water and protonation equilibrium of CO_3^{2-} ion govern the $p[H]$ of Na_2CO_3 solution.

$$\therefore K_w \cdot K_{a1} = [H^+][OH^-] \times \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = [H^+]^2[CO_3^{2-}]$$

$$\therefore \frac{1}{[H^+]} = \left(\frac{[CO_3^{2-}]}{K_w K_{a1}} \right)^{\frac{1}{2}}$$

$$K_{a1} = 5.6 \times 10^{-11}, \therefore pK_{a1} = 10.25, pK_w = 14, C = 0.189 M$$

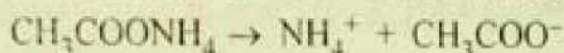
$$\therefore p[H] = \frac{1}{2} pK_w + \frac{1}{2} pK_{a1} + \frac{1}{2} \log[CO_3^{2-}]$$

$$= \frac{1}{2}(14) + \frac{1}{2}(10.25) + \frac{1}{2} \log(0.189) = 11.76$$

(v) **Salts containing acidic cation and basic anion (i.e, salts of weak acids with weak bases)**

Salts such as ammonium acetate (CH_3COONH_4), ammonium carbonate $(NH_4)_2CO_3$, sodium ammonium hydrogen phosphate, $[Na(NH_4)HPO_4]$, ammonium fluoride (NH_4F) etc. contain weakly acidic cation (NH_4^+) and basic anions, CH_3COO^- , CO_3^{2-} , HPO_4^{2-} and F^- respectively. $p[H]$ values of aqueous solutions of such salts depend upon the relative acid-base strengths of the cations and the anions.

(I) Ammonium acetate solution: The following are the principal reactions in the aqueous solution of ammonium acetate. The salt ionizes in aqueous solution completely,



The salt cation, NH_4^+ ion, ionizes as a weak acid releasing a proton,



The salt anion, CH_3COO^- ion, acting as a base, takes up the proton released by NH_4^+ ion,



Therefore, the net reaction involves proton transfer from the salt cation to the salt anion,



$$\therefore [CH_3COOH] = [NH_3],$$

$$\text{and } [NH_4^+] = [CH_3COO^-].$$

Ionization equilibrium of water has practically no contribution to the H^+ ion concentration of the solution, since, $K_w = 10^{-14}$, is much smaller than K_{CH_3COOH} and K_{NH_4} . $p[H]$ of ammonium acetate solution is governed by the protonation-deprotonation equilibria of acetate ion and ammonium ion only. Thus,

$$K_{CH_3COOH} \times K_{NH_4} = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \times \frac{[H^+][NH_3]}{[NH_4^+]} = [H^+]^2$$

$$\frac{1}{[H^+]} = \left(\frac{1}{K_{CH_3COOH}} \cdot \frac{1}{K_{NH_4}} \right)^{\frac{1}{2}}$$

$$\therefore K_{CH_3COOH} = 1.8 \times 10^{-5}, \quad \therefore pK_{CH_3COOH} = 4.74$$

$$\therefore K_{NH_4} = 5.5 \times 10^{-10}, \quad \therefore pK_{NH_4} = 9.26$$

$$\begin{aligned} \therefore p[H] &= \frac{1}{2} pK_{CH_3COOH} + \frac{1}{2} pK_{NH_4} \\ &= \frac{1}{2} (4.74) + \frac{1}{2} (9.26) = 7.0 \end{aligned}$$

Thus, aqueous solution of ammonium acetate will be neutral ($p[H] = 7$)

(2) Ammonium fluoride solution: (cf. Example 2.14 (2))



$$\therefore [HF] = [NH_3]$$

$$\therefore K_{NH_4} \cdot K_{HF} = \frac{[H^+][NH_3]}{[NH_4^+]} \times \frac{[H^+][F^-]}{[HF]} = [H^+]^2$$

$$\therefore [NH_4^+] = [F^-]$$

$$\therefore p[H] = \frac{1}{2} pK_{NH_4} + \frac{1}{2} pK_{HF}$$

$$(\because pK_{NH_4} = 9.26, \quad pK_{HF} = 3.46)$$

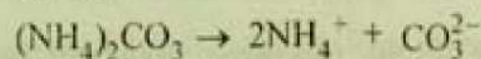
$$= \frac{1}{2} (9.26) + \frac{1}{2} (3.46) = 6.36$$

Therefore, ammonium fluoride solution will be slightly acidic ($pH < 7$)

(3) Ammonium carbonate solution

Principal reactions in ammonium carbonate solution are:

Ionization of the salt,



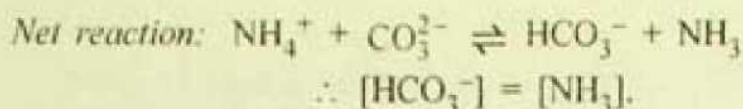
$$\therefore [NH_4^+] = 2[CO_3^{2-}]$$

Deprotonation of NH_4^+ ion,



Protonation of CO_3^{2-} ion,





Since $K_w = 10^{-14}$ is much smaller than K_{NH_4} and K_{HCO_3} , ionization equilibrium of H_2O molecules will have negligible contribution to the H^+ ion concentration of ammonium carbonate solution. $p[\text{H}]$ of this solution will be governed by the protonation - deprotonation equilibria of CO_3^{2-} and NH_4^+ ions respectively. Thus,

$$K_{\text{NH}_4} \cdot K_{\text{HCO}_3} = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} \times \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{[\text{H}^+]^2 \cdot [\text{CO}_3^{2-}]}{[\text{NH}_4^+]} = \frac{[\text{H}^+]^2}{2}$$

$$\frac{1}{[\text{H}^+]} = \left(\frac{1}{2 \cdot K_{\text{NH}_4} \cdot K_{\text{HCO}_3}} \right)^{\frac{1}{2}}$$

$$\therefore p[\text{H}] = \frac{1}{2} pK_{\text{NH}_4} + \frac{1}{2} pK_{\text{HCO}_3} - \frac{1}{2} \log 2$$

$$= \frac{1}{2} (pK_{\text{NH}_4} + pK_{\text{HCO}_3} - 0.3)$$

$$= \frac{1}{2} (9.26 + 10.25 - 0.3) = 9.605 = 9.61$$

Thus, ammonium carbonate solution will be distinctly alkaline ($p[\text{H}] > 7$).

So, the acidic or alkaline nature of aqueous solutions of salts of weak acids with weak bases will depend upon the relative acid-base strengths of the salt cations and salt anions. Acid strength of a cation is determined by its deprotonation constant (K_a), whereas, the basic strength of a salt anion is determined by its protonation constant (K_b), which is equal to K_w/K_a of the conjugate acid of the salt anion. Thus,

<i>Acid strength</i>	<i>Base strength</i>
----------------------	----------------------

Salt cation > conjugate base or salt anion	$p[\text{H}] < 7$ acidic solution
---	-----------------------------------

Salt cation $\approx$ conjugate base or salt anion ...	$p[\text{H}] \approx 7 \approx$ neutral solution
--	--

Salt cation < conjugate base or salt anion ...	$p[\text{H}] > 7$ alkaline solution
--	-------------------------------------

Problem (2.1)

Predict whether the aqueous solutions of the following salts will be acidic, neutral or alkaline.

(i) NH_4Br , [K_a of $\text{NH}_4^+ = 5.5 \times 10^{-10}$]

(ii) 0.01 M FeCl_3 , [$K_{\text{Fe}^{III}}^{\text{H}} = 6.3 \times 10^{-3}$]

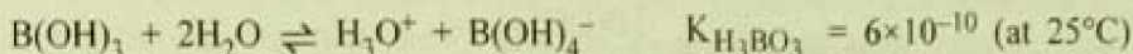
(iii) 0.02 M NaCN , [K_a of $\text{HCN} = 4.9 \times 10^{-10}$]

(iv) 0.2 M NaNO_2 , [K_a of $\text{HNO}_2 = 4.5 \times 10^{-5}$]

(v) 0.1 M Borax , [K_a of $\text{H}_3\text{BO}_3 = 6.0 \times 10^{-10}$]

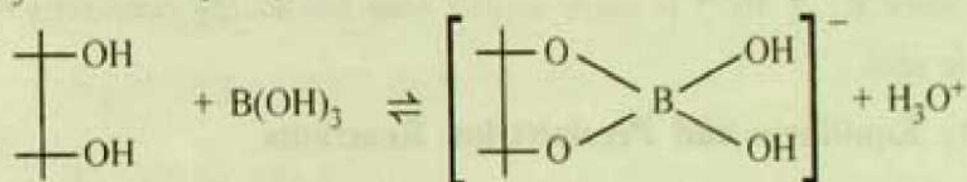
(vi) $p[H]$ of borate buffer solution

Boric acid, H_3BO_3 ($\equiv B(OH)_3$) is moderately soluble in water at ordinary temperature. Its solubility increases markedly with rise of temperature. Boric acid in aqueous solution is a very weak monobasic acid, that acts not as a proton donor (*Brönsted acid*), but as a *Lewis acid*, by accepting a OH^- ion from H_2O molecule:

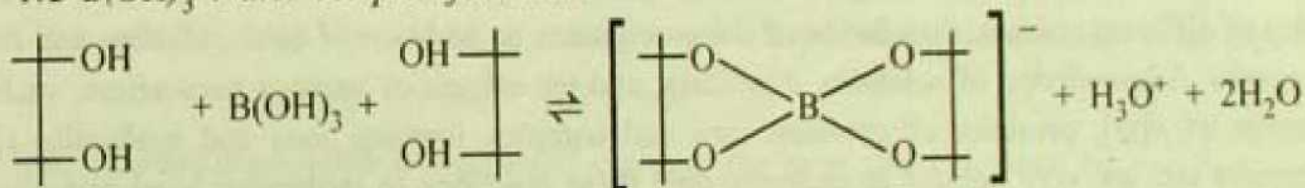


Acidity of boric acid solution is greatly enhanced in presence of 1, 2-*cis* diols, such as, 1, 2 glycol, glycerol, mannitol, catechol, etc., and 2-hydroxycarboxylic acids such as salicylic acid, due to chelate complex formation, arising from the profound tendency of B (+3) to achieve 4-coordination.

1:1 $B(OH)_3$: diol complex formation

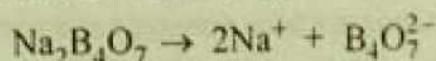


1:2 $B(OH)_3$: diol complex formation

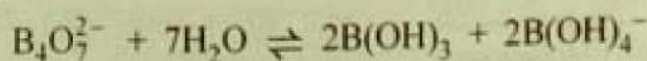


Stability constant of 1:2 boric acid-mannitol complex was determined to be $K = 1.7 \times 10^{-4}$ by Boeseken *et.al* (1930). The mononuclear species, $B(OH)_3$ and $B(OH)_4^-$ prevail in dilute solutions ($\leq 0.025 \text{ mol. lit}^{-1}$). Polynuclear species are formed in concentrated solutions. Boric acid-borate buffer mixtures serve as *standard buffer solutions*. Standard borate buffer solution of $p[H] = 9.22$ (at $25^\circ C$) may be conveniently prepared by dissolving borax, $Na_2B_4O_7 \cdot 10H_2O$ in water. $p[H]$ of this buffer solution is independent of concentration of borax, since in aqueous solution, tetraborate, $B_4O_7^{2-}$ ion, degrades into equimolar amounts of boric acid $B(OH)_3$ and borate $B(OH)_4^-$ anion. The principal reactions in aqueous solution of borax are:

Complete ionization of the salt,



Hydrolytic degradation of tetraborate ($B_4O_7^{2-}$) ion,



$$\therefore [B(OH)_3] = [B(OH)_4^-]$$

Since, the solution is now composed of an equimolar mixture of a weak acid, $B(OH)_3$ and its (salt) anion, $B(OH)_4^-$, it constitutes a buffer solution, $p[H]$ of which is given by *Henderson-Hasselbalch* equation,

$$\begin{aligned}
 p[H] &= pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \\
 &= pK_{H_3BO_3} + \log \frac{[B(OH)_4^-]}{[B(OH)_3]} \\
 &= pK_{H_3BO_3} \quad (\because [B(OH)_4^-] = [B(OH)_3]) \\
 &= -\log K_{H_3BO_3} = -\log(6 \times 10^{-10}) = 9.22 \quad (\text{at } 25^\circ\text{C})
 \end{aligned}$$

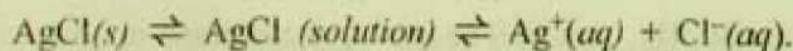
Ionization of water has practically no contribution to the hydrogen ion concentration of this solution, since $K_w = 10^{-14}$ is much smaller than the acidity constant ($K_{H_3BO_3} = 6 \times 10^{-10}$) of boric acid.

2.2 Solubility Equilibria and Precipitation Reactions

(a) Solubility Product Constant

Most chemical reactions in qualitative inorganic analysis involve the formation of precipitates of different colours, dissolution of the precipitates on addition of acids, alkalies and other reagents. A knowledge of solubility equilibria, and the effects of various parameters, such as change of $p[H]$, presence of common ions and complex forming ions and molecules (i.e., *ligands*) etc. are very helpful in understanding these reactions in molecular level and also in designing experimental conditions for precipitation of a particular compound, separation of a particular ion from a mixture with other ions by precipitation of a sparingly soluble compound.

Let us consider the solubility equilibrium of silver chloride ($AgCl$), which is sparingly soluble in water. If a small amount of solid silver chloride, $AgCl(s)$ is mixed with water and the mixture is shaken, small amount of the salt passes into solution because of its inherent solubility and the dissolved silver chloride, $AgCl$ (*solution*), ionizes completely to $Ag(aq)^+$ and $Cl^-(aq)$ ions, so that an equilibrium is established among solid silver chloride, silver chloride in solution and hydrated ions arising from ionization of dissolved silver chloride:



This equilibrium exists in a saturated solution of silver chloride. *Activity* of solid $AgCl(s)$ is unity and is constant, so is the activity of $AgCl(solution)$ as it is in equilibrium with $AgCl(s)$. Therefore, the activities of $Ag^+(aq)$ and $Cl^-(aq)$ ions are also constant at a particular temperature. The equilibrium constant of this ionization equilibrium may be defined as,

$$K = \frac{a_{Ag^+(aq)} \cdot a_{Cl^-(aq)}}{a_{AgCl(solution)}}$$

where 'a's stand for the activities of the respective species.

$$\therefore K.a_{\text{AgCl (solution)}} = a_{\text{Ag}^+ (\text{aq})} \cdot a_{\text{Cl}^- (\text{aq})} = \text{constant}$$

Substituting $K_{\text{sp}} = K.a_{\text{AgCl (solution)}}$, one obtains,

$$K_{\text{sp}} = a_{\text{Ag}^+ (\text{aq})} \cdot a_{\text{Cl}^- (\text{aq})} = \text{Constant}$$

K_{sp} , which is the product of activities of $\text{Ag}^+ (\text{aq})$ and $\text{Cl}^- (\text{aq})$ ions in a saturated solution of AgCl , i.e., when the ions $\text{Ag}^+ (\text{aq})$ and $\text{Cl}^- (\text{aq})$ are in equilibrium with solid $\text{AgCl}(s)$, at a particular temperature, is a constant at that temperature, and is called the *solubility product constant* or simply *solubility product* of silver chloride. For a sparingly soluble salt, such as silver chloride, even the saturated solution is almost infinitely dilute, and the *activity coefficients* are close to unity, so the activities of the constituent ions may be replaced by their respective concentrations, consequently, a *concentration solubility product*, K_{sp} , may be defined as the product of concentrations of the constituent ions in a saturated solution of a sparingly soluble salt. Thus, for silver chloride,

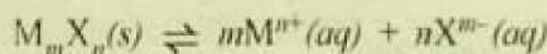
$$K_{\text{sp}} = [\text{Ag}^+ (\text{aq})] \cdot [\text{Cl}^- (\text{aq})]$$

or, simply,

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

omitting the term (aq) for simplicity.

For a sparingly soluble salt, M_mX_n , the general solubility equilibrium may be written as,



The concentration solubility product, omitting the term (aq) , is given by,

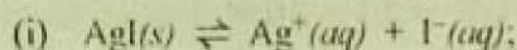
$$K_{\text{sp}} = [\text{M}^{n+}]^m [\text{X}^{m-}]^n$$

Thus, solubility product (K_{sp}) is equal to the product of equilibrium concentrations of all the ions produced in the saturated solution of a sparingly soluble salt (i.e., electrolyte) with concentration of each ion raised to the power of its coefficient in the balanced chemical equation representing the solubility equilibrium.

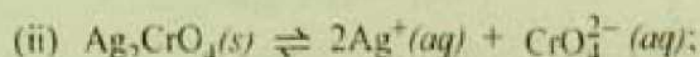
Examples (2.17)

(i) Write the solubility equilibria and the expressions for solubility products, of the following:

(i) AgI , (ii) Ag_2CrO_4 , (iii) $\text{Fe}(\text{OH})_3$, (iv) Bi_2S_3 , (v) $\text{Ca}_3(\text{PO}_4)_2$.



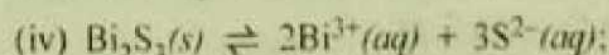
$$K_{\text{sp}} = [\text{Ag}^+][\text{I}^-]$$



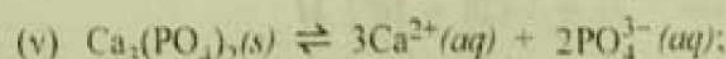
$$K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$$



$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3$$



$$K_{\text{sp}} = [\text{Bi}^{3+}]^2[\text{S}^{2-}]^3$$

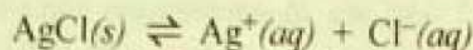


$$K_{\text{sp}} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

From a knowledge of the solubility product of a compound at a particular temperature, it is possible to calculate the equilibrium concentrations of the constituent ions in a saturated solution of the sparingly soluble salt at that temperature, provided there is no side reaction.

Examples (2.18)

- (1) Solubility product of silver chloride is 1.8×10^{-10} at 25°C . What is the concentration of silver ion in a saturated solution of this salt at this temperature?

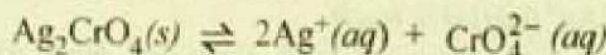


$$\therefore [\text{Ag}^+] = [\text{Cl}^-]$$

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+]^2$$

$$\therefore [\text{Ag}^+] = (K_{sp})^{\frac{1}{2}} = (1.8 \times 10^{-10})^{\frac{1}{2}} = 1.34 \times 10^{-5} \text{ (M)}$$

- (2) Solubility product of silver chromate at 25°C is 1.1×10^{-12} . What is the concentration of chromate ion in a saturated solution of silver chromate at this temperature?



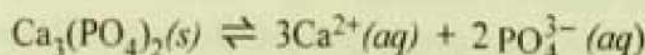
$$\therefore [\text{Ag}^+] = 2[\text{CrO}_4^{2-}]$$

$$K_{sp} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}] = (2[\text{CrO}_4^{2-}])^2[\text{CrO}_4^{2-}] = 4[\text{CrO}_4^{2-}]^3 = 1.1 \times 10^{-12}$$

$$\therefore [\text{CrO}_4^{2-}] = \left(\frac{1.1 \times 10^{-12}}{4} \right)^{\frac{1}{3}} = 6.5 \times 10^{-5} \text{ (M)}$$

- (3) Solubility product of calcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$ is 2.1×10^{-33} at 25°C . What is the solubility of this salt at this temperature?

If solubility of $\text{Ca}_3(\text{PO}_4)_2$ is $x \text{ mol.lit}^{-1}$, then concentration of Ca^{2+} ion and PO_4^{3-} ion in a saturated solution of this salt will be $3x$ and $2x \text{ mol.lit}^{-1}$ respectively, according to its solubility equilibrium:



1 mol.	3 moles	2 moles
$x \text{ mole}$	$3x \text{ moles}$	$2x \text{ moles}$

$$\therefore \text{Solubility product, } K_{sp} = (3x)^3(2x)^2 = (3)^3(2)^2(x)^5 = 2.1 \times 10^{-33}$$

$$\therefore x = \left(\frac{2.1 \times 10^{-33}}{(3)^3(2)^2} \right)^{\frac{1}{5}} = \left(\frac{2.1 \times 10^{-33}}{108} \right)^{\frac{1}{5}} = 1.142 \times 10^{-7} \text{ M}$$

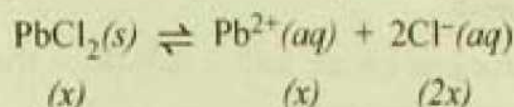
$$\therefore \text{Molar solubility of } \text{Ca}_3(\text{PO}_4)_2 = x = 1.142 \times 10^{-7} \text{ M}$$

$$\text{Equilibrium concentration of } \text{Ca}^{2+} \text{ ion} = 3x = 3.426 \times 10^{-7} \text{ M}$$

$$\text{Equilibrium concentration of } \text{PO}_4^{3-} \text{ ion} = 2x = 2.284 \times 10^{-7} \text{ M}$$

(b) Effect of Common Ions on the Solubility of Sparingly Soluble Salts

In the discussion of acid-base equilibria we have seen that in presence of strong acids (such as HCl, HNO₃) which ionize completely in aqueous solution, producing equivalent amounts of H⁺ ion, the ionization equilibria of weak acids (such as acetic acid, hydrofluoric acid etc.) are depressed. Let us now see, how the solubility of a sparingly soluble salt is influenced by the presence of a common ion. Let us consider the solubility equilibrium of lead chloride, PbCl₂, which is precipitated on addition of dilute hydrochloric acid solution to an aqueous solution of a soluble lead salt, in Group-I of systematic group analysis (cf. Sect 4.4, 7.8).



$$K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.2 \times 10^{-5} \text{ at } 25^\circ\text{C}.$$

If $x \text{ mol.lit}^{-1}$ be the molar solubility of the salt, then in a saturated solution of PbCl₂, the equilibrium concentrations of Pb²⁺ and Cl⁻ ions are respectively x and $2x \text{ mol.lit}^{-1}$.

$$\therefore K_{sp} = (x)(2x)^2 = 4x^3 = 1.2 \times 10^{-5}$$

$$\therefore [\text{Pb}^{2+}] = x = \left(\frac{1.2 \times 10^{-5}}{4} \right)^{\frac{1}{3}} = 1.44 \times 10^{-2} M$$

$$\therefore [\text{Cl}^-] = 2x = 2.88 \times 10^{-2} M$$

Suppose, to a saturated solution of PbCl₂ some (say 0.1 mol.lit^{-1}) sodium chloride (NaCl) is added. Because of complete ionization, NaCl produces 0.1 mol.lit^{-1} of the Cl⁻ ion, which is a common ion of PbCl₂. Under this condition the new concentration of chloride ion will be, $(2x + 0.1) \text{ mol.lit}^{-1}$, which is much larger than the Cl⁻ ion concentration in the saturated solution of PbCl₂ in absence of sodium chloride. Since the solubility product (K_{sp}) is a constant at a particular temperature, equilibrium concentration of Pb²⁺ ion, hence, the solubility of PbCl₂, will diminish accordingly.

$$\begin{aligned} K_{sp} &= [\text{Pb}^{2+}][\text{Cl}^-]^2 = (x)(2x + 0.1)^2 = 1.2 \times 10^{-5} \\ \therefore &= (x)(2.88 \times 10^{-2} + 0.1)^2 = 1.2 \times 10^{-5} \\ \therefore x &= 7.23 \times 10^{-4} M \end{aligned}$$

Similarly if $0.1 M$ lead nitrate solution is added to the saturated solution of PbCl₂, Pb²⁺ produced by lead nitrate exerts common ion effect and lowers the solubility of PbCl₂.

$$\begin{aligned} K_{sp} &= [\text{Pb}^{2+}][\text{Cl}^-]^2 = 1.2 \times 10^{-5} \\ \therefore [\text{Pb}^{2+}] &= 1.44 \times 10^{-2} (M) \end{aligned}$$

Therefore, after addition of the salt,

$$\begin{aligned} (1.44 \times 10^{-2} + 0.1)(2x)^2 &= 1.2 \times 10^{-5} \\ \therefore x &= 5.12 \times 10^{-3} M \end{aligned}$$

Problem (2.2)

- (1) Calculate the molar solubility of MgF_2 ($K_{sp} = 7.4 \times 10^{-11}$ at 25°C)
 (i) in absence and (ii) in presence of 0.1 M MgCl_2 solution.

It appears, therefore, that, solubilities of sparingly soluble salts are diminished in presence of electrolytes producing common ions, provided that the common ions do not participate in any side reaction, such as complex formation, formation of compounds of stoichiometry other than the parent sparingly soluble salt. Such a phenomenon is called *common ion effect*.

(c) Coprecipitation and Post Precipitation

The phenomenon of contamination of a precipitate with a substance that is soluble under the condition of precipitation is called *coprecipitation*.

Examples (2.19)

- (i) $\text{Fe}(\text{OH})_3$, during its precipitation, may drag down $\text{Zn}(\text{OH})_2$ if Zn^{2+} is also present in the solution along with Fe^{3+} .
 (ii) Calcium oxalate precipitate may be contaminated with calcium hydroxide, sodium oxalate.
 (iii) $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$ may drag down $\text{Ni}^{2+}(\text{aq})$ and $\text{Ni}(\text{NH}_3)_6^{2+}$ ions.

On the other hand, contamination of an impurity after precipitation of the desired compound in pure form is termed as *post precipitation*. This occurs if a precipitate is allowed to stand in the solution containing slightly soluble analogous compounds containing a common ion.

Examples (2.20)

(i) CuS is precipitated in pure form when precipitated from a solution containing both Cu^{2+} and Zn^{2+} ions in $0.2\text{--}0.3 \text{ N}$ acid medium. Since under this condition only the solubility product of CuS is exceeded, whereas, that of ZnS is not exceeded (e.g. K_{sp} value at 25°C of CuS and ZnS are 6×10^{-36} and 1.6×10^{-24} respectively). But if the precipitate of CuS is kept in contact with the solution containing Zn^{2+} and H_2S , then the precipitate of CuS is slowly contaminated with ZnS .

Other examples of post precipitation include: precipitation of ZnS and NiS (precipitated in ammoniacal medium) on HgS and Bi_2S_3 which are precipitated in strongly acidic medium, precipitation of FeS on CuS and precipitation of magnesium oxalate on calcium oxalate.

Coprecipitation and post precipitation may involve

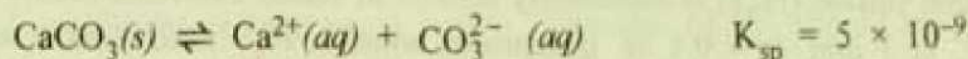
- Substitution of one ion by another of the same kind in the crystal lattice of the precipitate.
- Adsorption of the impurity on the surface of the precipitate.
- Occlusion i.e., physical trapping of the mother liquor containing the impurity.
- Mutual precipitation of suspended colloidal particles.

The degree of contamination by either of the above processes, of course, depends upon the concentration of the foreign materials. The extent of contamination is decreased considerably at lower concentration of the impurities. Precipitation under hot condition or at boiling condition

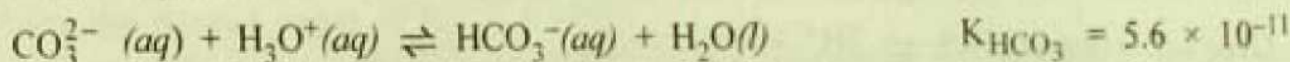
favours faster coagulation of the precipitate, consequently the extent of contamination of impurity is lower.

(d) Effect of $p[H]$ on Solubilities of Salts

Solubilities of sparingly soluble metal salts derived from weak acids are often influenced by $p[H]$ of the solution. In general, solubility increases with lowering of $p[H]$ (i.e., increase of acidity) of the solution. This is because, the anions (i.e., the conjugate bases) of the weak acids, generated in the solubility equilibria of the salts, tend to strongly bind with the protons, as a result, the solubility equilibria are right shifted in favour of the anions, consequently solubilities increase. Let us consider the solubility equilibrium of calcium carbonate, CaCO_3 ($K_{sp} = 5 \times 10^{-9}$ at 25°C):



CO_3^{2-} ion, being the conjugate base of the weak acid (HCO_3^-), combines with a proton to form HCO_3^- ion,



So, the net reaction is,



As CO_3^{2-} ions are removed from the solubility equilibrium of $\text{CaCO}_3(s)$, more and more $\text{CaCO}_3(s)$ dissolve to restore and maintain the solubility equilibrium.

In qualitative inorganic analysis, we often come across salts whose solubility and precipitation from solution are strongly influenced by $p[H]$ of the solution. Such compounds are sulfides, hydroxides, carbonates, phosphates, borates, silicates, fluorides etc. In systematic group separation of cations, we come across various types of precipitation reactions which are $p[H]$ dependent. These are discussed in the following sections.

(e) Precipitation of Sulfides

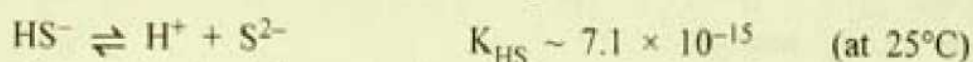
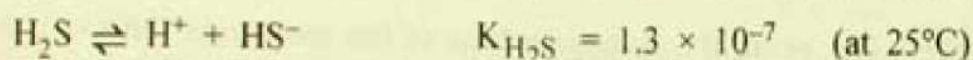
Copper and Arsenic group metal sulfides (Group-IIA and IIB of systematic group separation) are precipitated in acidic solution ($[\text{HCl}] \approx 0.1 \text{ M}$), whereas, the Zn-group metal sulfides (Group-IIIB of systematic group separation) are precipitated in $\text{NH}_4\text{Cl} - \text{NH}_3$ buffer medium ($p[H] \approx 10$). Consideration of the solubility products (expressed in pK_{sp} values Table 2.3) of some metal sulfides of these groups will reveal that a comparatively lower sulfide (S^{2-}) ion concentration, as available in a saturated solution of H_2S ($[\text{H}_2\text{S}] = 0.1 \text{ M}$), (in acid medium, $[\text{HCl}] = 0.1 \text{ M}$) is sufficient to exceed the solubility products of the copper and arsenic group metal sulfides, leading to their precipitation, keeping the Zn-group metals in solution. Precipitation of Zn-group metal sulfides occur at much higher concentration of S^{2-} ion, as available in ammoniacal/alkaline solution, ($\text{NH}_4\text{Cl} - \text{NH}_3$ buffer, $p[H] = 10$).

Table 2.3: Solubility products (pK_{sp} values at 25°C) of some metal sulfides

<i>Copper and arsenic group metal sulfides</i>				<i>Zinc group metal sulfides</i>	
CuS	35.2	As ₂ S ₃	28.4	ZnS	23.8
CdS	26.1	SnS	25	CoS	20.4
PbS	26.6	Sb ₂ S ₃	92.8	NiS	24.0
Cu ₂ S	47.6	Bi ₂ S ₃	97	MnS	9.6

(i) Precipitation of sulfides with H₂S - water

Hydrogen sulfide (H₂S) is moderately soluble in water. Saturated solution of H₂S in water at $20-25^\circ\text{C}$ at 1 atm. is $\approx 0.1\text{ M}$. In aqueous solution H₂S ionizes as a weak diprotic acid,



Over all reaction: $\text{H}_2\text{S} \rightleftharpoons 2\text{H}^+ + \text{S}^{2-}$

$$\therefore K_{\text{H}_2\text{S}} \cdot K_{\text{HS}} = \frac{[\text{H}^+][\text{HS}^-]}{[\text{H}_2\text{S}]} \times \frac{[\text{H}^+][\text{S}^{2-}]}{[\text{HS}^-]} = \frac{[\text{H}^+]^2[\text{S}^{2-}]}{[\text{H}_2\text{S}]}$$

$\therefore$ Sulfide (S^{2-}) ion concentration in a saturated solution of H₂S ($[\text{H}_2\text{S}] = 0.1\text{ M}$) will be,

$$[\text{S}^{2-}] = \frac{K_{\text{H}_2\text{S}} \cdot K_{\text{HS}} [\text{H}_2\text{S}]}{[\text{H}^+]^2} = \frac{(1.3 \times 10^{-7}) \cdot (7.1 \times 10^{-15}) \cdot 0.1}{[\text{H}^+]^2} \approx \frac{10^{-22}}{[\text{H}^+]^2} \text{ M}$$

As the S^{2-} ion concentration shows inverse square dependence on H^+ ion concentration, metal sulfides with lower solubility products (higher pK_{sp} values) will precipitate at lower S^{2-} ion concentration as available in acidic solution and those with higher values of solubility products (lower pK_{sp} values) will precipitate at higher sulfide ion concentration, as available in alkaline (ammoniacal) medium.

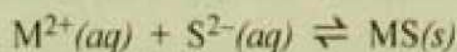
In 0.1 M HCl medium: $[\text{H}^+] = 0.1\text{ M}$,

$$[\text{S}^{2-}] = \frac{10^{-22}}{(0.1)^2} = 10^{-20} \text{ M}$$

In $\text{NH}_4\text{Cl-NH}_3$ buffer solution: $p[\text{H}] = 10$, $[\text{H}^+] = 10^{-10}\text{ M}$

$$[\text{S}^{2-}] = \frac{10^{-22}}{(10^{-10})^2} = 10^{-2} \text{ M}$$

Let us calculate the hydrogen ion concentration or $p[\text{H}]$ of precipitation of a metal sulfide (MS) from a solution, in which the concentration of the metal ion is $C\text{ mol.lit}^{-1}$, by treating the solution with H₂S. At the end of precipitation, the metal sulfide, metal ion and sulfide ion remain in equilibrium, which is essentially the solubility equilibrium of the metal sulfide, written in the opposite direction:



The solubility product (K_{MS}) of the metal sulfide is given by,

$$K_{MS} = [M^{2+}][S^{2-}]$$

The completeness of precipitation may be expressed by a parameter, called *recovery factor* (R_M), which may be defined according to,

$$R_M = \frac{\text{Quantity of M precipitated}}{\text{Original quantity of M}} = \frac{C - [M^{2+}]}{C}$$

$$\therefore [M^{2+}] = C(1 - R_M)$$

where, $[M^{2+}]$ = equilibrium concentration of $[M^{2+}]$ ion in solution left behind even after precipitation. For an ideal separation, $[M^{2+}] \rightarrow 0$ and so, $R_M \rightarrow 1$. For establishing the condition for almost complete precipitation of the metal sulfide, the value of R_M should be chosen as close to 1 as possible. Suppose for a particular separation, the required value of $R_M = 0.999$. To accommodate the experimental errors, impurities in the reagents, uncertainties in the values of the physical constants used, one should aim at a still higher value of R_M , e.g. $R_M = 0.9999$, to achieve the desired value of $R_M = 0.999$.

Substituting the values of $[S^{2-}]$ and $[M^{2+}]$ in the expression of solubility product, one obtains,

$$K_{MS} = C(1 - R_M) \cdot \frac{10^{-22}}{[H^+]^2}$$

$$[H^+] = \left[\frac{C(1 - R_M) \cdot 10^{-22}}{K_{MS}} \right]^{\frac{1}{2}}$$

$$\frac{1}{[H^+]} = \left(\frac{K_{MS} \cdot 10^{22}}{C(1 - R_M)} \right)^{\frac{1}{2}}$$

For a macro analysis $R_M \approx 0.999$. To achieve $R_M = 0.999$, one has to aim at a higher value of $R_M = 0.9999$ (say). If the concentration (C) of the metal ion is $10^{-2} \text{ mol.lit}^{-1}$, then,

$$C(1 - R_M) = 10^{-2}(1 - 0.9999) = 10^{-2} \cdot 10^{-4} = 10^{-6}$$

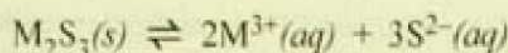
Denoting the $[H^+]$ under this condition as $[H^+]_{10^{-6}}$, one obtains,

$$\therefore \frac{1}{[H^+]_{10^{-6}}} = \left(\frac{K_{MS} \cdot 10^{22}}{10^{-6}} \right)^{\frac{1}{2}} = (K_{MS} \cdot 10^{28})^{\frac{1}{2}}$$

Therefore, $p[H]_{10^{-6}}$ of complete precipitation of the metal sulfide (MS) will be

$$p[H]_{10^{-6}} = 14 - \frac{1}{2} pK_{MS}$$

Similarly for a metal sulfide of the formula, M_2S_3 , for which the solubility equilibrium is,

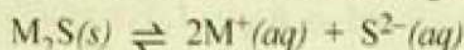


$$K_{M_2S_3} = [M^{3+}]^2[S^{2-}]^3$$

it may be shown that,

$$p[H]_{10^{-6}} = 13 - \frac{1}{6} pK_{M_2S_3}$$

and for a metal sulfide of the formula, M_2S , for which the solubility equilibrium is,



$$K_{M_2S} = [M^{+}]^2[S^{2-}]$$

$$p[H]_{10^{-6}} = 17 - \frac{1}{2} pK_{M_2S}$$

Thus, it is possible to calculate the $p[H]_{10^{-6}}$ of precipitation of different metal sulfides using these relations if the solubility products of the sulfides are known.

Table (2.4): $[pH]_{10^{-6}}$ of precipitation of some metal sulfides.

M_xS_y	$pK_{M_xS_y}$	$p[H]_{10^{-6}}$ or $[H^{+}]_{10^{-6}}$
SnS	25	1.5
CdS	26	1 = 0.1 M
ZnS	24.1	2
MnS	12.6	7.7
CoS	20.4	3.8
FeS	17.2	5.4
Co_2S_3	24	9
PbS	26.6	0.7
Tl_2S	20.3	6.85
CuS	35.5	– $10^4 M^*$
Bi_2S_3	97	– $10^3 M^*$

* These are all calculated values, and are improbable, but these mean high concentration of H^{+} ion.

It is, therefore, possible to precipitate one metal ion as its sulfide keeping even another metal ion of the same group in solution by properly maintaining the acidity or $p[H]$ of the solution. A specific example is capillary separation of Cu^{2+} and Cd^{2+} ion on a filter paper by precipitation of their sulfides at different acidity (*cf.* Sect. 7.8). Although both CuS (black)

and CdS (yellow) are precipitated in dilute hydrochloric acid medium $[HCl] = 0.1 \sim 0.3 M$, for complete precipitation of CdS, acidity should be $0.1 M$ or lower, but complete precipitation of CuS occurs even at much higher acidity than this.

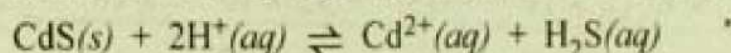
Now, if a filter paper is spotted with drops of a solution containing both Cu^{2+} and Cd^{2+} ions in dilute HCl ($\sim 0.1 M$) medium, and then a drop of H_2S -water is added, a black spot appears. Although both CuS (black) and CdS (yellow) are precipitated, only the black colour of CuS is visible, as the yellow colour of CdS is completely masked by the black colour of CuS. Alternatively, the filter paper may be spotted with a freshly precipitated white slurry of zinc sulfide (ZnS) and then a drop of the weakly acidic/neutral or ammoniacal solution of a mixture of Cu^{2+} and Cd^{2+} ions may be added, when a black spot due to CuS is observed.



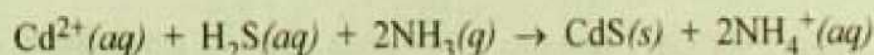
($M = Cu, Cd$).

Since the solubility product of ZnS ($K_{ZnS} \approx 10^{-24}$) is much higher than the solubility products of CuS ($K_{CuS} \approx 3.2 \times 10^{-36}$) and CdS ($K_{CdS} \approx 10^{-26}$), in acidic medium ZnS passes into solution leaving sufficient S^{2-} ion concentration for precipitation of CuS and CdS.

Now if a solution of (1:1) dilute HCl (i.e. $6 M$ HCl) is held on the black spot using a capillary dropper, the black spot remains as such, as CuS does not dissolve in the HCl solution. But CdS partly dissolves in the HCl solution and a colourless moist ring containing $Cd^{2+}(aq)$ ion and $H_2S(aq)$ moves outward by capillary action, the black spot remaining at the center.



After the moist ring has moved away a reasonable distance from the black spot, if the paper is held over ammonia gas, a yellow coloured spot due to CdS appears out side the black spot of CuS.



Problem (2.3)

A solution which is $0.01 M$ in $CuCl_2$ and $CdCl_2$ in $5M$ HCl, is saturated with H_2S gas at $25^\circ C$. What % of CuS and CdS will be precipitated? [Given: $K_{CuS} = 3.2 \times 10^{-36}$, $K_{CdS} = 1 \times 10^{-26}$ at $25^\circ C$]

Solution:

$[H^+]$ ion concentration required to be maintained for precipitation of a metal sulfide (MS) is given by,

$$[H^+] = \left[\frac{C(1 - R_M)10^{-22}}{K_{MS}} \right]^{\frac{1}{2}}$$

where, K_{MS} = solubility product of MS, C = original concentration of the metal ion in solution and R_M = recovery factor which is a measure of completeness of precipitation. R_M

is defined by, $R_M = (C - [M^{2+}])/C$, where, $[M^{2+}]$ = equilibrium concentration of the metal ion in solution, even after precipitation of MS.

$$\therefore (1 - R_M) = \frac{[H^+]^2 \cdot K_{MS} \cdot 10^{22}}{C}$$

For Cd^{2+} : $C = 0.01 \text{ M}$, for CdS ($K_{CdS} = 10^{-26}$),

$$\therefore (1 - R_M) = \frac{[H^+]^2 \cdot 10^{-26} \cdot 10^{22}}{10^{-2}} = [H^+]^2 \times 10^{-2}$$

Since HCl is a strong acid, it is completely ionized in aqueous solution,

$$\therefore [H^+] = [HCl] = 5M$$

$$\therefore (1 - R_M) = (5)^2 \times 10^{-2} = 0.25$$

$$\therefore R_M = 0.75$$

$$\therefore R_M\% = R_M \times 100 = 75\%$$

$\therefore$ 75% of Cd^{2+} will precipitate as CdS and 25% of Cd^{2+} will remain in solution.

For CuS ($K_{CuS} = 3.2 \times 10^{-36}$)

$$\therefore (1 - R_M) = \frac{[H^+]^2 \times K_{CuS} \times 10^{22}}{C} = \frac{(5)^2 \times 3.2 \times 10^{-36} \times 10^{22}}{10^{-2}} = 25 \times 10^{-12}$$

$$\therefore R_M = 1 - 25 \times 10^{-12} \approx 1$$

$$\therefore R_M\% \approx 100\%$$

Therefore, when 25% Cd^{2+} remains in solution, CuS is precipitated almost to the extent of 100%.

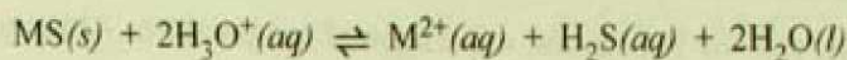
[$\therefore R_M = \frac{C - [Cu^{2+}]}{C} = 1$, $\therefore C - [Cu^{2+}] = C$, i.e. $[Cu^{2+}] \approx 0$. That is, concentration of Cu^{2+} in solution will be practically zero.]

(ii) Separation of metal ions by selective precipitation of sulfides

If a reagent, added to a mixture of cations, reacts selectively with certain cations to produce sparingly soluble compounds while leaving the others in solution, separation of the cations from their mixtures may be possible through such reactions. In the systematic group separation of cations, when dilute HCl is added to the solution containing a mixture of $AgNO_3$ and $CuSO_4$, curdy white precipitate of $AgCl$ appears in Group-I, whereas, Cu^{2+} ion remains in solution. If an acidic solution of $CuSO_4$ and $ZnSO_4$ is treated with H_2S -water, only black precipitate of CuS appears in Group-II leaving Zn^{2+} ions in solution. Zn^{2+} is also precipitated as white coloured ZnS , but not in acidic medium as in Group-II, but in ammoniacal medium in Group-IIIB. Similarly Pb^{2+} , Hg^{2+} , Cd^{2+} are precipitated as their sulfides in acidic medium in Group-

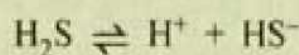


II, whereas, Mn^{2+} , Co^{2+} , Ni^{2+} are precipitated as sulfides in ammoniacal medium in Group-IIIB. This implies that the sulfides of Group-II metals are much less soluble in acidic medium than the sulfides of Group-IIIB metals. The separation of metal sulfides (MS) in acidic medium from their aqueous solutions is based on the magnitude of the equilibrium constant (K_{spa}) of the following solubility equilibrium,

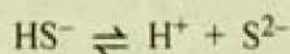


$$K_{spa} = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2}$$

The constant, K_{spa} , called the *solubility product in acid*, is related to the traditional solubility product, K_{sp} , of metal sulfide (MS) through the ionization constants (K_2^H and K_1^H) of H_2S in aqueous solution:



$$K_2^H = \frac{[H^+][HS^-]}{[H_2S]}$$

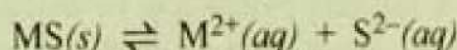


$$K_1^H = \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$\therefore K_1^H K_2^H = \frac{[H^+]^2 [S^{2-}]}{[H_2S]}$$

$$\therefore [S^{2-}] = K_1^H K_2^H [H_2S] / [H^+]^2$$

For the traditional solubility equilibrium,



the traditional solubility product (K_{sp}) is given by,

$$K_{sp} = [M^{2+}][S^{2-}].$$

Substituting for $[S^{2-}]$, one obtains,

$$K_{sp} = \left(\frac{[M^{2+}][H_2S]}{[H^+]^2} \right) K_1^H K_2^H = K_{spa} \cdot K_1^H \cdot K_2^H$$

$$\therefore K_{spa} = \frac{K_{sp}}{K_1^H K_2^H}$$

The traditional solubility product, K_{sp} , in its definition, involves the equilibrium concentrations of the metal ion (M^{2+}) and that of the fully deprotonated form of H_2S , i.e. $[S^{2-}]$ ion. But the concentration of S^{2-} ion in a saturated solution of H_2S in water, depends upon the analytical concentration of H^+ ion in the solution and the values of successive deprotonation constants K_2^H and K_1^H of H_2S at the experimental temperature. Although precise value of K_2^H is experimentally determinable, there is, a lot of uncertainty on the reported values of K_1^H , which range from 1.3×10^{-14} to $\sim 10^{-19}$. Such a small value of K_1^H implies that S^{2-} ion is strongly basic, like O^{2-} ion and as such it is not an important species in aqueous solution. The constant, K_{spa} , on the other hand, involves the analytical concentrations of the metal ion (M^{2+}), unionised dissolved H_2S molecules $[H_2S]$, and hydrogen ion, $[H^+]$ or $[H_3O^+]$. K_{spa} in fact, is a *practical constant*, and is more useful in predicting the possibility of separation of metal ions by precipitation of their sulfides*. Separation of sulfides of course, depends upon the adjustment of H_3O^+ ion concentration, so that the magnitude of the reaction quotient (Q_c , where the subscript 'c' implies concentration quotient) exceeds K_{spa} for very insoluble sulfides, but not for the more soluble ones.

Example (2.21)

(1) If 0.01 M solution of a metal ion (M^{2+}) in 0.3 M HCl medium is saturated with H_2S gas providing $[H_2S] = 0.1$ M, the reaction quotient (Q_c) will be,

$$Q_c = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2} = \frac{(0.01)(0.1)}{(0.3)^2} \approx 1.11 \times 10^{-2}$$

From a comparison of this value of Q_c with the K_{spa} values at 25°C of some Group-II and Group IIIB metal sulfides given below, it will be evident why the Group II metal sulfides are precipitated in acidic medium, but the Group-IIIB metal ions remain in solution under this condition.

Metal sulfides (Group-II)

MS	$K_{spa} < Q_c$
HgS	2×10^{-32}
PbS	3×10^{-7}
CuS	6×10^{-16}

(Precipitated in acidic solution)

Metal sulfides (Group-IIIB)

MS	$K_{spa} > Q_c$
MnS	3×10^{10}
CoS	4×10^{-1}
NiS	8×10^{-1}

(Not precipitated in acidic solution)

Problem (2.4)

(1) K_{spa} values of CdS and ZnS at 25°C are 8×10^{-7} and 3×10^{-2} respectively. What

* R. J. Myers, J. Chem. Educ., 1986, 63, 687-690.

will be the observation if a solution, which is 0.005 M in Cd^{2+} and 0.005 M in Zn^{2+} in 0.3 M HCl medium is saturated with H_2S gas providing $[\text{H}_2\text{S}] = 0.1\text{ M}$?

$$(Q_c) = \frac{(0.005)(0.1)}{(0.3)^2} = 5.56 \times 10^{-3}$$

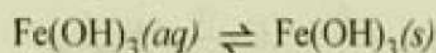
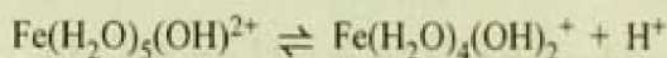
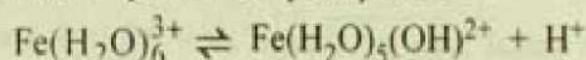
$$\therefore (K_{\text{spa}})\text{CdS} < Q_c < (K_{\text{spa}})\text{ZnS}$$

Therefore, yellow precipitate of CdS will appear, leaving Zn^{2+} ion in solution.

(f) Effect of $p[\text{H}]$ on the Precipitation of Metal Hydroxides

(i) $p[\text{H}]$ of precipitation of metal hydroxides

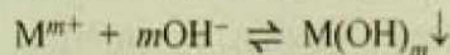
In qualitative inorganic analysis we come across several metal ions which form sparingly soluble hydroxides. Mostly the metal ions of high charge and small size (i.e. those with high ionic potentials) strongly polarize the $\text{O}-\text{H}$ bonds of coordinated H_2O molecules, eventually leading to deprotonation of the hydrated metallic ion. In section (2.1.f) dealing with $p[\text{H}]$ of aqueous solutions of salts, we have seen that aqueous solutions containing, $\text{Fe}(\text{H}_2\text{O})_6^{3+}$, $\text{Al}(\text{H}_2\text{O})_6^{3+}$ etc. ions are fairly acidic due to deprotonation of coordinated water molecules. With successive deprotonation of a hydrated metallic ion, its charge gradually decreases and eventually electroneutral hydroxides precipitate:



Increase of $p[\text{H}]$ (i.e., decrease of H^+ ion concentration), therefore, favours the precipitation of metallic hydroxides.

Since the solubility products of hydroxides of common metal ions differ widely (Appendix-A4), this offers a means of qualitative identification and also quantitative separation of metal ions by precipitation of their hydroxides by adjustment of $p[\text{H}]$ of the solution.

Let us first find the $p[\text{H}]$ of complete precipitation of a metal ion, M^{m+} , as its hydroxide, $\text{M}(\text{OH})_m$. The precipitation equilibrium of the hydroxide is,



Solubility product $(K_{\text{sp}})_M$ of the metal hydroxide, $\text{M}(\text{OH})_m$, is defined as,

$$(K_{\text{sp}})_M = [\text{M}^{m+}] [\text{OH}^-]^m$$

If the initial analytical concentration of the metal ion is C_M (mol.lit^{-1}), and M^{m+} is the only form in which the metal ion can exist in solution, then the fraction of the metal ion precipitated as hydroxide, (i.e., the recovery factor) R_M , will be equal to,

$$R_M = \frac{C_M - [\text{M}^{m+}]}{C_M}$$

$$\therefore [\text{M}^{m+}] = C_M(1 - R_M)$$

where, $[M^{m+}]$ is the equilibrium concentration of M^{m+} ion in solution even after precipitation. Substituting this value of $[M^{m+}]$ and of $[OH^-] = K_w/[H^+]$, one obtains,

$$(K_{sp})_M = C_M(1 - R_M) \cdot (K_w / [H^+])^m$$

$$\therefore \frac{1}{[H^+]} = \frac{1}{K_w} \cdot [(K_{sp})_M]^{\frac{1}{m}} \cdot [C_M(1 - R_M)]^{-\frac{1}{m}}$$

$$\therefore p[H] = pK_w - \frac{1}{m} p(K_{sp})_M - \frac{1}{m} \log C_M(1 - R_M)$$

For a typical analysis, $C_M \approx 10^{-2}$ (mol.lit⁻¹), the recovery factor R_M should be ≈ 0.999 . To achieve this value of R_M , a still higher value, say $R_M \approx 0.9999$ should be aimed at to accommodate the uncertainty in the literature values of the constants used, errors in $p[H]$ measurement and impurities in the reagents used.

Therefore, $C_M(1 - R_M) = 10^{-2}(1 - 0.9999) = 10^{-2} \cdot 10^{-4} = 10^{-6}$. If the $p[H]$ value signifying this condition be $p[H]_{10^{-6}}$, then,

$$p[H]_{10^{-6}} = pK_w - \frac{1}{m} p(K_{sp})_M + \frac{6}{m}$$

At 25°C, $pK_w = 14$, therefore, $p[H]_{10^{-6}}$ values for almost quantitative ($\sim 99.99\%$) precipitation of the hydroxides of metal ions of charge $m = +2, +3$ and $+4$ will be,

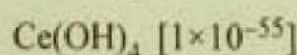
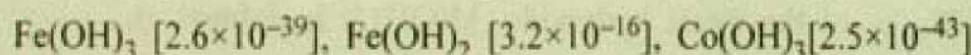
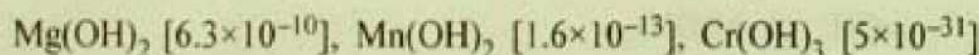
$$m = +2 \quad p[H]_{10^{-6}} = 14 - \frac{1}{2} p(K_{sp})_M + \frac{6}{2} = 17 - \frac{1}{2} p(K_{sp})_M$$

$$m = +3 \quad p[H]_{10^{-6}} = 14 - \frac{1}{3} p(K_{sp})_M + \frac{6}{3} = 16 - \frac{1}{3} p(K_{sp})_M$$

$$m = +4 \quad p[H]_{10^{-6}} = 14 - \frac{1}{4} p(K_{sp})_M + \frac{6}{4} = 15.5 - \frac{1}{4} p(K_{sp})_M$$

Problem (2.5)

Find the $p[H]_{10^{-6}}$ of precipitation of the following metal hydroxides of which the solubility products at 25°C are given in the square brackets [].



(ii) Precision of $p[H]$ adjustment for precipitation of metal hydroxides

In actual analysis, when a metal ion (M^{m+}) solution is treated with a base, precipitation is initiated when $p[H]$ of the solution rises to certain value at which the solubility product of the metal hydroxide, $M(OH)_m$, is just exceeded. As the OH^- ions are removed due to precipitation of the metal hydroxide, no further precipitation can occur until additional amount

of the base is added, i.e., the $p[H]$ is further increased. Again, in presence of a large excess of alkali, certain metal hydroxides, (e.g. $Al(OH)_3$, $Zn(OH)_2$, $Pb(OH)_2$ etc.), because of their *amphoteric* nature, dissolve in excess alkali, producing hydroxo complexes. It is, therefore, important to add just sufficient base, so that precipitation of the desired hydroxide is complete (i.e, recovery factor $R_M \approx 1$), without any side reaction leading to its dissolution. To establish such a condition, the $p[H]$ of the solution should be increased from the $p[H]$ of incipient precipitation ($R_M \approx 0$) to a $p[H]$ of complete precipitation, at which $R_M \approx 1$, more appropriately, $R_M \approx 0.9999$. If $[H^+]_{R_M=0}$ and $[H^+]_{R_M=0.9999}$ be the hydrogen ion concentrations of the solution for incipient precipitation and complete precipitation respectively, then,

$$\frac{\frac{1}{[H^+]_{R_M=0.9999}}}{\frac{1}{[H^+]_{R_M=0}}} = \frac{\frac{[(K_{sp})_M]^{\frac{1}{m}}}{K_w(C_M)^{\frac{1}{m}} \cdot \frac{1}{(1-0.9999)^{\frac{1}{m}}}}}{\frac{[(K_{sp})_M]^{\frac{1}{m}}}{K_w(C_M)^{\frac{1}{m}} \cdot \frac{1}{(1-0)^{\frac{1}{m}}}}} = \frac{1}{(10^{-4})^{\frac{1}{m}}} = 10^{\frac{4}{m}}$$

Taking logarithm on both sides, one obtains,

$$\log_{10} \frac{1}{[H^+]_{R_M=0.9999}} - \log_{10} \frac{1}{[H^+]_{R_M=0}} = 4 / m$$

$$\therefore p[H]_{R_M=0.9999} - p[H]_{R_M=0} = \Delta p[H] = 4 / m$$

Therefore, the extent to which the $p[H]$ of the solution has to be increased ($\Delta p[H]$), from the $p[H]$ of incipient precipitation to achieve complete precipitation, depends upon the metal ion charge. For metal ions of charge +2, +3 and +4, the $\Delta p[H]$ values will be as follows:

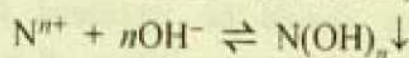
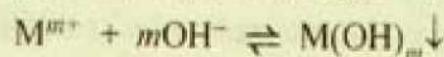
m	+2	+3	+4
$\Delta p[H] = 4/m$	2	1.33	1

(iii) Separation of metal ions by precipitation of hydroxides

When the solubility products of the hydroxides of two metal ions are widely different, it is often possible to precipitate one metal as its hydroxide keeping the other metal ion in solution. Suppose, we have two metal ions in a mixture, the desired one, M^{m+} , of concentration C_M ($mol.lit.^{-1}$) and an undesired one, N^{n+} , of concentration C_N ($mol.lit.^{-1}$). Solubility products of the two hydroxides $M(OH)_m$ and $N(OH)_n$ be $(K_{sp})_M$ and $(K_{sp})_N$ respectively, so that $(K_{sp})_M < (K_{sp})_N$. Since the solubility product of $M(OH)_m$ is less than that of $N(OH)_n$, the former will precipitate at lower OH^- ion concentration (i.e., at lower $p[H]$) than the latter. We are to find

the relation between $(K_{sp})_M$ and $(K_{sp})_N$, so that, when $M(OH)_m$ is completely precipitated ($R_M \approx 1$, more appropriately $R_M = 0.9999$), the total of N^{n+} remains in solution (i.e., $R_N = 0$).

Precipitation equilibria of the two hydroxides are,



Solubility products of the two hydroxides $(K_{sp})_M$ and $(K_{sp})_N$ are defined as,

$$(K_{sp})_M = [M^{m+}][OH^-]^m$$

$$(K_{sp})_N = [N^{n+}][OH^-]^n$$

If M^{m+} be the only form in which the metal M exists in solution, then the recovery factor R_M of the desired metal ion M^{m+} is defined as,

$$R_M = \frac{C_M - [M^{m+}]}{C_M}$$

$$\therefore [M^{m+}] = C_M(1 - R_M)$$

where, $[M^{m+}]$ = equilibrium concentration of M^{m+} in solution even after precipitation.

$$\therefore (K_{sp})_M = C_M(1 - R_M)[OH^-]^m$$

$$\therefore [OH^-] = \left[\frac{(K_{sp})_M}{C_M(1 - R_M)} \right]^{\frac{1}{m}}$$

This is the concentration of OH^- ion required for complete precipitation ($R_M = 0.9999$) of $M(OH)_m$.

For no precipitation of $N(OH)_n$, ($R_N = 0$), at this OH^- ion concentration, the necessary condition is,

$$[N^{n+}] \times [OH^-]^n \leq (K_{sp})_N$$

that is,

$$(K_{sp})_N \geq [N^{n+}] \cdot \left[\frac{(K_{sp})_M}{C_M(1 - R_M)} \right]^{\frac{n}{m}}$$

If N^{n+} is the only form in which the metal N can exist in the solution, then its equilibrium concentration, $[N^{n+}]$, may be taken as equal to its total analytical concentration, C_N (mol.lit^{-1}). Therefore,

$$(K_{sp})_N \geq C_N \times \left[\frac{(K_{sp})_M}{C_M(1 - R_M)} \right]^{\frac{n}{m}}$$

$$\therefore \frac{(K_{sp})_N}{[(K_{sp})_M]^{\frac{n}{m}}} \geq \frac{C_N}{[C_M(1 - R_M)]^{\frac{n}{m}}}$$

For metal ions of same charge type, $m = n$, $(n/m) = 1$

$$\therefore \frac{(K_{sp})_N}{(K_{sp})_M} \geq \frac{C_N}{C_M(1 - R_M)}$$

For a mixture of two metal ions at the same concentration, $C_M = C_N$,

$$\therefore \frac{(K_{sp})_N}{(K_{sp})_M} \geq \frac{1}{1 - R_M}$$

If the concentration of the undesired metal ions, N^{n+} , is 10 times the concentration of the desired metal ion, M^{m+} , i.e., $C_N = 10 C_M$.

$$\frac{(K_{sp})_N}{(K_{sp})_M} \geq \frac{10}{1 - R_M}$$

For a typical analysis,

if $C_M = 10^{-2} \text{ (mol.lit}^{-1}\text{)}$, $C_N = 1 \text{ (mol.lit}^{-1}\text{)}$, $m \neq n$, $R_M = 0.9999$,

$$\frac{(K_{sp})_N}{[(K_{sp})_M]^{\frac{n}{m}}} \geq \frac{1}{[10^{-2}(1 - 0.9999)]^{\frac{n}{m}}} = \frac{1}{[10^{-2} \cdot 10^{-4}]^{\frac{n}{m}}} = 10^{6n/m}$$

$$\therefore \left(\frac{n}{m}\right) p(K_{sp})_M - p(K_{sp})_N \geq 6n/m$$

for a system with $m = n$, $(n/m) = 1$

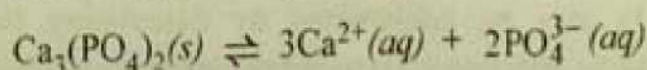
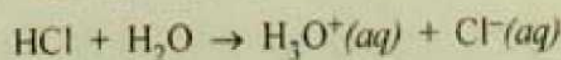
$$p(K_{sp})_M - p(K_{sp})_N \geq 6$$

Problem (2.6)

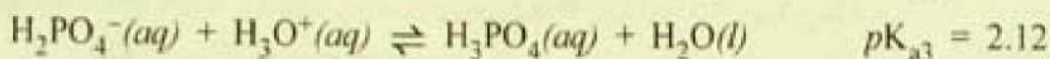
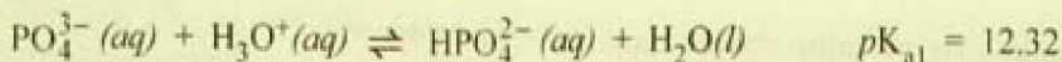
Test the feasibility of separation of the metal ions Fe^{3+} , Cr^{3+} and Mg^{2+} from their mixture by precipitation of their hydroxides. [Given: $(K_{sp})_{\text{Fe}} = 2.6 \times 10^{-39}$, $(K_{sp})_{\text{Cr}} = 5 \times 10^{-31}$, $(K_{sp})_{\text{Mg}} = 6.3 \times 10^{-10}$ at 25°C]

(g) Effect of $p[\text{H}]$ on Precipitation of Phosphates

Phosphates of most metals, other than those of the alkali metals and the ammonium salts, are sparingly soluble in water, but dissolve in dilute solutions of mineral acids (HCl , HNO_3 , H_2SO_4). Since phosphoric acid (H_3PO_4) is a weak triprotic acid (*cf.* Sect 2.1.e), phosphate ion (PO_4^{3-}) (i.e. the conjugate base of phosphoric acid) acts as a strong base. In presence of completely ionized mineral acids, phosphate is protonated in stepwise manner producing successively HPO_4^{2-} , H_2PO_4^- and ultimately H_3PO_4 :



$$pK_{sp} = 32.68$$



As the acidity of the solution is gradually lowered, (i.e. $p[\text{H}]$ is increased) the concentrations of H_2PO_4^- , HPO_4^{2-} and PO_4^{3-} ions gradually increase, as a result, solubility products of metallic phosphates are exceeded, and the phosphate salts are precipitated. In alkaline or ammoniacal medium, most metallic phosphates (other than those of Na^+ , K^+ , NH_4^+) are precipitated. Phosphates of some metals [e.g., $\text{Ti}(\text{IV})$, $\text{Zr}(\text{IV})$, $\text{Th}(\text{IV})$] are precipitated even in acidic solutions. With $\text{Fe}(\text{III})$ and $\text{Al}(\text{III})$, hydroxides are also precipitated at the $p[\text{H}]$ of precipitation of their phosphates.

Concentration of various phosphate species at different $p(\text{H})$ may be viewed from the species distribution curves of phosphoric acid (Fig. 2.1), which show that H_3PO_4 and H_2PO_4^- dominate the region below $p[\text{H}]$ 4, H_2PO_4^- and HPO_4^{2-} dominate the region between $p[\text{H}]$ 4 to 10 and the region above $p[\text{H}]$ 10 is dominated by PO_4^{3-} ion.

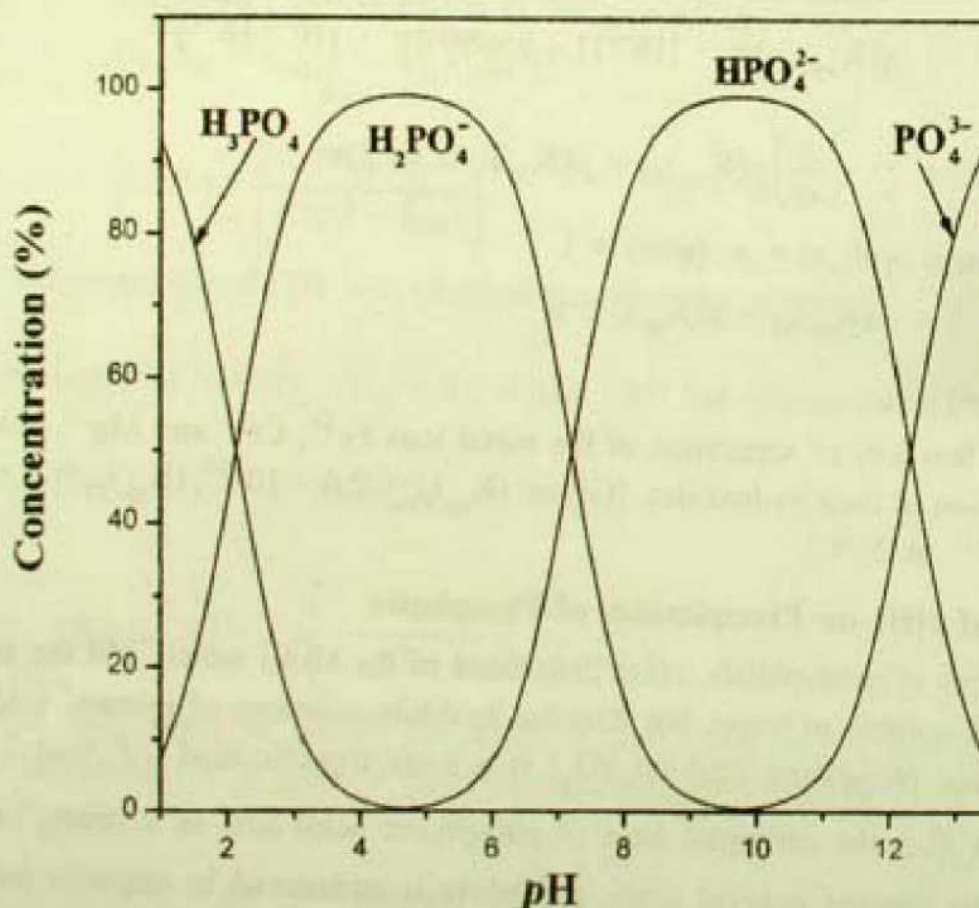


Fig. 2.1. Speciation of phosphoric acid species as a function of $p[\text{H}]$. (for H_3PO_4 : $pK_{a3} = 2.12$, $pK_{a2} = 7.21$, $pK_{a1} = 12.32$ at 25°C)

The speciation curves (Fig 2.1) may be constructed by calculating the equilibrium concentrations of the phosphate species at different $p[\text{H}]$ using the ionization constants of H_3PO_4

and then plotting the concentration (%) against $p[H]$. If C (mol.lit^{-1}) be the total concentration of phosphoric acid species, then at equilibrium,

$$C = [\text{PO}_4^{3-}] + [\text{HPO}_4^{2-}] + [\text{H}_2\text{PO}_4^-] + [\text{H}_3\text{PO}_4]$$

$$= [\text{PO}_4^{3-}] \left(1 + \frac{[\text{H}^+]}{K_{a1}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} + \frac{[\text{H}^+]^3}{K_{a1}K_{a2}K_{a3}} \right)$$

where, K_{a1} , K_{a2} , K_{a3} are the first, second and third protonation constants of PO_4^{3-} ion i.e. the third, second and first deprotonation constants of H_3PO_4 .

$$\therefore [\text{PO}_4^{3-}] = \frac{C}{1 + \frac{[\text{H}^+]}{K_{a1}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} + \frac{[\text{H}^+]^3}{K_{a1}K_{a2}K_{a3}}}$$

$$\therefore [\text{PO}_4^{3-}](\%) = \frac{100}{1 + \frac{[\text{H}^+]}{K_{a1}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} + \frac{[\text{H}^+]^3}{K_{a1}K_{a2}K_{a3}}} = \frac{100}{1 + x + y + z}$$

$$\text{where, } x = \frac{[\text{H}^+]}{K_{a1}} = \text{Inverse log } (pK_{a1} - p[H]) = \text{Inverse log } (12.32 - p[H])$$

$$y = \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} = \text{Inverse log } (pK_{a1} + pK_{a2} - 2p[H]) = \text{Inverse log } (19.53 - 2p[H])$$

$$z = \frac{[\text{H}^+]^3}{K_{a1}K_{a2}K_{a3}} = \text{Inverse log } (pK_{a1} + pK_{a2} + pK_{a3} - 3p[H]) = \text{Inverse log } (21.65 - 3p[H])$$

Since K_{a1} , K_{a2} and K_{a3} are known, $[\text{PO}_4^{3-}]$ % in the solution may be calculated by using these relations from a knowledge of the pH of the solution.

Once the $[\text{PO}_4^{3-}]$ % at a $p[H]$ is known, the concentration (%) of the protonated phosphate species may be calculated using the following relations:

$$[\text{HPO}_4^{2-}]\% = \frac{[\text{H}^+]}{K_{a1}} \cdot [\text{PO}_4^{3-}]\% = x[\text{PO}_4^{3-}]\%$$

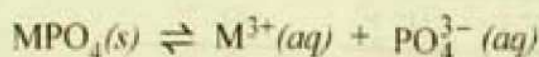
$$[\text{H}_2\text{PO}_4^-]\% = \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} \cdot [\text{PO}_4^{3-}]\% = y[\text{PO}_4^{3-}]\%$$

$$[\text{H}_3\text{PO}_4]\% = \frac{[\text{H}^+]^3}{K_{a1}K_{a2}K_{a3}} \cdot [\text{PO}_4^{3-}]\% = z[\text{PO}_4^{3-}]\%$$

In qualitative inorganic analysis, identifying tests of metallic radicals are required to be

conducted in acidic, neutral as well as in ammoniacal (or alkaline) medium. If phosphate ion is present, it does not interfere severely in the tests conducted in acidic medium, since, in acid medium, dominant phosphate species is the unionized molecules of H_3PO_4 . As the acidity of the solution is lowered, proportions of deprotonated phosphoric acid species gradually increase, eventually solubility products of many metallic phosphates are exceeded leading to precipitation of their phosphates, and this is how phosphate interferes the detection of metal ions in neutral as well as in ammoniacal medium.

$p[\text{H}]$ of precipitation of different phosphates may be calculated in the same manner as the precipitation of metallic sulfides and hydroxides (*cf.* Sect. 2.2.e., 2.2.f.). Solubility equilibria of the phosphates (MPO_4) of a trivalent metal ion (e.g. Fe^{3+} , Al^{3+} , Cr^{3+} , Co^{3+} , Mn^{3+}), may be expressed as,



The solubility product, K_{sp} , is defined as,

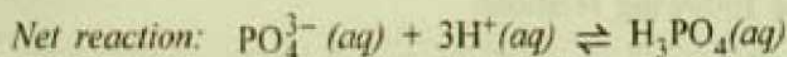
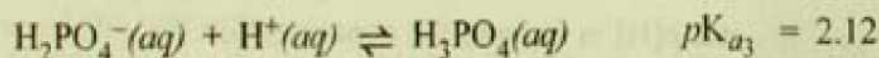
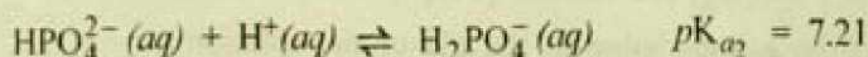
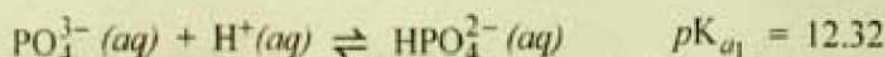
$$K_{sp} = [\text{M}^{3+}][\text{PO}_4^{3-}]$$

If C_M be the initial concentration of M^{3+} ions in solution, and if M^{3+} is the only form in which the metal ion exists in solution and $\text{MPO}_4(s)$ be the only compound that is preprecipitated from the solution, then the extent (or, completeness) of precipitation (i.e. recovery factor), R_M , may be defined as,

$$R_M = \frac{C_M - [\text{M}^{3+}]}{C_M}$$

$$\therefore [\text{M}^{3+}] = C_M(1 - R_M)$$

The PO_4^{3-} ion is also involved in protonation equilibria according to,



These are just the opposite reactions of deprotonation equilibria of protonated phosphate species (*cf.* p-25). For the net protonation equilibrium,

$$K_{a1} \cdot K_{a2} \cdot K_{a3} = \frac{[\text{H}^+]^3[\text{PO}_4^{3-}]}{[\text{H}_3\text{PO}_4]}$$

$$\therefore [\text{PO}_4^{3-}] = \frac{K_{a1} \cdot K_{a2} \cdot K_{a3}[\text{H}_3\text{PO}_4]}{[\text{H}^+]^3}$$

Substituting the values of $[M^{3+}]$ and $[PO_4^{3-}]$ ions in the solution even after precipitation in the expression for K_{sp} , one obtains,

$$K_{sp} = \frac{C_M(1 - R_M) \cdot K_{a1} K_{a2} K_{a3} [H_3PO_4]}{[H^+]^3}$$

$$\therefore \frac{1}{[H^+]} = \left(\frac{K_{sp}}{C_M(1 - R_M) K_{a1} K_{a2} K_{a3} [H_3PO_4]} \right)^{\frac{1}{3}}$$

$$\therefore p[H] = \frac{1}{3} (pK_{a1} + pK_{a2} + pK_{a3}) - \frac{1}{3} pK_{sp} - \frac{1}{3} \log C_M(1 - R_M)[H_3PO_4]$$

For a typical analysis, let $C_M \approx 10^{-2} M$ and the required value of $R_M = 0.999$. To achieve this value of R_M , a still higher value of R_M i.e., $R_M = 0.9999$ should be aimed at to accommodate the uncertainties in the values of the constants, K_{a1} , K_{a2} and K_{a3} ; impurities in the reagents and errors in the $p[H]$ measurement. Thus,

$$C_M(1 - R_M) = 10^{-2} \cdot (1 - 0.9999) = 10^{-2} \cdot 10^{-4} = 10^{-6}$$

$$\text{For } H_3PO_4, K_{a1} \cdot K_{a2} \cdot K_{a3} = 10^{-12.32} \cdot 10^{-7.21} \cdot 10^{-7.12} = 10^{-21.65}$$

$$\therefore pK_{a1} + pK_{a2} + pK_{a3} = 21.65$$

$$\therefore C_M(1 - R_M) K_{a1} K_{a2} K_{a3} = 10^{-6} \cdot 10^{-21.65} = 10^{-27.65}$$

If the H^+ ion concentration under this condition be denoted by $[H^+]_{10^{-6}}$, then,

$$\therefore \frac{1}{[H^+]_{10^{-6}}} = \left(\frac{K_{sp}}{10^{-27.65} \cdot [H_3PO_4]} \right)^{\frac{1}{3}} = \left(\frac{K_{sp} \cdot 10^{27.65}}{[H_3PO_4]} \right)^{\frac{1}{3}}$$

$$\therefore p[H]_{10^{-6}} = 9.22 - \frac{1}{3} pK_{sp} - \frac{1}{3} \log[H_3PO_4]$$

Thus, the H^+ ion concentrations required for precipitation of the phosphate salts depend upon their solubility products and the equilibrium concentration of H_3PO_4 , i.e., indirectly on the PO_4^{3-} ion concentration.

$$\text{If } [H_3PO_4] = 0.01M = 10^{-2} M$$

$$p[H]_{10^{-6}} = 9.22 - \frac{1}{3} pK_{sp} - \frac{1}{3} \log(0.01)$$

$$= 9.22 - \frac{1}{3} (-2) - \frac{1}{3} pK_{sp}$$

$$\therefore p[H]_{10^{-6}} = 9.89 - \frac{1}{3} pK_{sp}$$

Similarly, if $[H_3PO_4] = 0.1 \text{ M} = 10^{-1} \text{ M}$.

$$p[H] = 9.22 - \frac{1}{3} \log(0.1) - \frac{1}{3} pK_{sp} = 9.22 - \frac{1}{3} (-1) - \frac{1}{3} pK_{sp}$$

$$\therefore p[H] = 9.55 - \frac{1}{3} pK_{sp}$$

Thus, at lower concentration of H_3PO_4 , precipitation of phosphate will occur at higher $p[H]$.

Example (2.22)

(1) At what $p[H]$ will $FePO_4$ precipitate to the extent of 99.99% from a 0.01 M solution of Fe^{3+} , if the concentration of H_3PO_4 in the solution is (i) 0.01 M, (ii) 0.10 M? [Given: solubility product of $FePO_4 = 1.3 \times 10^{-22}$ and K_{a1} , K_{a2} and K_{a3} of H_3PO_4 are 4.79×10^{-13} , 6.17×10^{-8} and 7.59×10^{-3} respectively at 25°C]

$$K_{sp} = 1.3 \times 10^{-22}$$

$$\therefore pK_{sp} = 21.89$$

$$K_{a1} = 4.79 \times 10^{-13}$$

$$\therefore pK_{a1} = 12.32$$

$$K_{a2} = 6.17 \times 10^{-8}$$

$$\therefore pK_{a2} = 7.21$$

$$K_{a3} = 7.59 \times 10^{-3}$$

$$\therefore pK_{a3} = 2.12$$

$$\therefore pK_{a1} + pK_{a2} + pK_{a3} = 12.32 + 7.21 + 2.12 = 21.65$$

$$p[H] = \frac{1}{3} (pK_{a1} + pK_{a2} + pK_{a3}) - \frac{1}{3} pK_{sp} - \frac{1}{3} \log C_M(1 - R_M)[H_3PO_4]$$

$$\text{Now, } C_{Fe}(1 - R_{Fe}) = 10^{-2} \cdot 10^{-4} = 10^{-6}$$

$$\text{For } FePO_4, pK_{sp} = 21.89$$

$$\therefore p[H] = \frac{1}{3} (21.65) - \frac{1}{3} (21.89) - \frac{1}{3} \log 10^{-6} [H_3PO_4]$$

$$p[H] = 1.92 - \frac{1}{3} \log[H_3PO_4]$$

$$\text{For } [H_3PO_4] = 0.01 \text{ M}$$

$$p[H] = 1.92 - \frac{1}{3} \log(0.01) = 1.92 - \frac{1}{3} \log 10^{-2} = 1.92 + \frac{2}{3} = 2.59$$

$$\text{For } [H_3PO_4] = 0.1 \text{ M}$$

$$p[H] = 1.92 - \frac{1}{3} \log(0.1) = 1.92 - \frac{1}{3} \log(10^{-1}) = 1.92 + \frac{1}{3} = 2.25$$

Or, simply by applying the relations deduced above, one may obtain:

$$\text{For } [H_3PO_4] = 0.01 \text{ M}$$

$$p[H] = 9.89 - \frac{1}{3} \cdot 21.89 = 2.59$$

For $[H_3PO_4] = 0.1M$

$$p[H] = 9.55 - \frac{1}{3} \cdot 21.89 = 2.25$$

Problem (2.7)

(1) Solubility product of $AlPO_4$ is 5.75×10^{-19} . At what $p[H]$ will it precipitate to the extent of 99.99% from a 0.01 M solution of Al^{3+} , if the concentration of H_3PO_4 is (i) 0.01M and (ii) 0.10M? (Given: pK_{a1} , pK_{a2} , pK_{a3} of H_3PO_4 are 12.32, 7.21 and 2.12 respectively at 25°C).

$$pK_{a1} + pK_{a2} + pK_{a3} = 12.32 + 7.21 + 2.12 = 21.65$$

$$pK_{sp} = -\log_{10} K_{sp} = -\log_{10} 5.75 \times 10^{-19} = 18.24$$

$$C_{Al} = 10^{-2}M$$

$$R_{Al}\% = 99.99\%$$

$$\therefore R_{Al} = 0.9999$$

$$(1 - R_{Al}) = 1 - 0.9999 = 10^{-4}$$

$$\therefore C_{Al}(1 - R_{Al}) = 10^{-2} \cdot 10^{-4} = 10^{-6}$$

$p[H]_{10^{-6}}$ of precipitation is,

$$\begin{aligned} p[H]_{10^{-6}} &= \frac{1}{3}(pK_{a1} + pK_{a2} + pK_{a3}) - \frac{1}{3}pK_{sp} - \frac{1}{3}\log 10^{-6}[H_3PO_4] \\ &= \frac{1}{3}(21.65) - \frac{1}{3}(18.24) - \frac{1}{3}(\log 10^{-6}) - \frac{1}{3}(\log[H_3PO_4]) \\ &= 3.14 - \frac{1}{3}\log[H_3PO_4] \end{aligned}$$

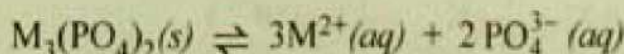
(i) For $[H_3PO_4] = 0.01 M$

$$p[H]_{10^{-6}} = 3.14 - \frac{1}{3}\log(0.01) = 3.81$$

(ii) For $[H_3PO_4] = 0.10M$

$$p[H]_{10^{-6}} = 3.14 - \frac{1}{3}\log(0.1) = 3.47$$

Solubility equilibria of bivalent metal phosphates, $M_3(PO_4)_2$, ($M = Pb^{2+}$, Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} etc.), may be represented as,



The solubility product of $M_3(PO_4)_2$ may be defined as,

$$K_{sp} = [M^{2+}]^3[PO_4^{3-}]^2$$

If M^{2+} is the only form in which the metal ion exists in solution, then the extent of precipitation (or, recovery factor), R_M , is given by,

$$R_M = \frac{C_M - [M^{2+}]}{C_M}$$

where, $[M^{2+}]$ is the equilibrium concentration of M^{2+} ion even after precipitation,

$$\therefore [M^{2+}] = C_M(1 - R_M)$$

Equilibrium concentration of PO_4^{3-} ion is given by,

$$[PO_4^{3-}] = \left(\frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H^+]^3} \right)$$

If $M_3(PO_4)_2$ is the only compound that is precipitated then,

$$K_{sp} = [C_M(1 - R_M)]^3 \times \left(\frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H^+]^3} \right)^2$$

For a typical analysis, $C_M = 10^{-2}M$

$R_M = 0.9999$ (for almost complete precipitation).

$$\therefore C_M(1 - R_M) = 10^{-2}(1 - 0.9999) = 10^{-6}$$

If H^+ ion concentration under this condition is $[H^+]_{10^{-6}}$, then,

$$\frac{1}{[H^+]_{10^{-6}}} = \left(\frac{K_{sp}}{(10^{-6})^3(K_{a1}K_{a2}K_{a3})^2[H_3PO_4]^2} \right)^{\frac{1}{6}}$$

$$\therefore p[H]_{10^{-6}} = 3 + \frac{1}{3}(pK_{a1} + pK_{a2} + pK_{a3}) - \frac{1}{6}pK_{sp} - \frac{1}{3}\log[H_3PO_4]$$

$$\therefore pK_{a1} + pK_{a2} + pK_{a3} = (12.32 + 7.21 + 2.12) = 21.65$$

$$\therefore p[H]_{10^{-6}} = 10.22 - \frac{1}{6}pK_{sp} - \frac{1}{3}\log[H_3PO_4]$$

For $[H_3PO_4] = 0.01M$

$$p[H]_{10^{-6}} = 10.22 - \frac{1}{6}pK_{sp} - \frac{1}{3}\log(10^{-2})$$

$$\therefore p[H]_{10^{-6}} = 10.88 - \frac{1}{6}pK_{sp}$$

For $[H_3PO_4] = 0.10M$

$$p[H]_{10^{-6}} = 10.22 - \frac{1}{6} pK_{sp} - \frac{1}{3} \log(10^{-1})$$

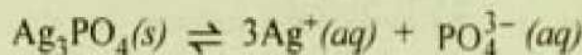
$$\therefore p[H]_{10^{-6}} = 10.55 - \frac{1}{6} pK_{sp}$$

$p[H]_{10^{-6}}$ of precipitation of some common bivalent metal phosphates for $[H_3PO_4] = 0.01M$ and $0.1M$ are calculated using the above equations (Table 2.5).

Table 2.5: $p[H]$ of precipitation of some bivalent metal phosphates, $M_3(PO_4)_2$.

$M_3(PO_4)_2$	$K_{sp} (25^\circ C)$	pK_{sp}	$p[H]_{10^{-6}}$	
			$[H_3PO_4] = 0.01M$	$[H_3PO_4] = 0.10M$
$Pb_3(PO_4)_2$	7.9×10^{-43}	42.1	3.86	3.53
$Zn_3(PO_4)_2$	9.1×10^{-33}	32.04	5.54	5.21
$Ca_3(PO_4)_2$	2×10^{-29}	28.70	6.10	5.77
$Mg_3(PO_4)_2$	1×10^{-13}	13.0	8.71	8.38

Solubility equilibria of monovalent metal phosphates, such as, Ag_3PO_4 , may be represented as,



$$K_{sp} = [Ag^+]^3 [PO_4^{3-}] = 1.3 \times 10^{-20} (25^\circ C).$$

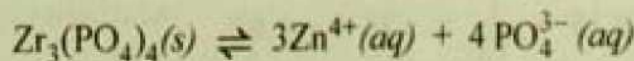
If $C_{Ag^+} = 0.01M$, $R_{Ag} = 0.9999$, one may obtain for $[H_3PO_4] = 0.01M$.

$$p[H]_{10^{-6}} = 13.88 - \frac{1}{3} pK_{sp} = 7.25$$

For $[H_3PO_4] = 0.10M$

$$p[H]_{10^{-6}} = 13.55 - \frac{1}{3} pK_{sp} = 6.92$$

For a tetravalent metal phosphate, such as, $Zr_3(PO_4)_4$, the solubility equilibria, assuming Zr^{4+} is the only form in which the metal ion exists in solution and $Zr_3(PO_4)_4$ is the only compound that precipitates, may be expressed as,



$$K_{sp} = [Zr^{4+}]^3 [PO_4^{3-}]^4$$

Recovery factor of Zr may be defined as,

$$R_{Zr} = \frac{C_{Zr} - [Zr^{4+}]}{C_{Zr}}$$

where, $[Zr^{4+}]$ is the equilibrium concentration of Zr^{4+} even after precipitation of $Zr_3(PO_4)_4$, and C_{Zr} is the initial concentration of Zr^{4+} .

$$\therefore K_{sp} = [C_{Zr}(1 - R_{Zr})]^3 \left(\frac{K_{a1}K_{a2}K_{a3}[H_3PO_4]}{[H^+]^3} \right)^4$$

For a typical analysis, $C_{Zr} = 10^{-2}M$

$R_{Zr} = 0.9999$ (for almost complete precipitation)

$$\therefore C_{Zr}(1 - R_{Zr}) = 10^{-2}(1 - 0.9999) = 10^{-6}$$

For H_3PO_4 , $K_{a1} \cdot K_{a2} \cdot K_{a3} = 10^{-12.32} \cdot 10^{-7.21} \cdot 10^{-2.12} = 10^{-21.65}$

$$\therefore K_{sp} = (10^{-6})^3 \left(\frac{10^{-21.65} \cdot [H_3PO_4]}{[H^+]_{10^{-6}}^3} \right)^4$$

$$= 10^{-18} \cdot 10^{-86.6} \cdot \left(\frac{[H_3PO_4]}{[H^+]_{10^{-6}}^3} \right)^4$$

$$= 10^{-104.6} \cdot \frac{[H_3PO_4]^4}{[H^+]_{10^{-6}}^{12}}$$

$$\therefore p[H]_{10^{-6}} = 8.72 - \frac{1}{12} pK_{sp} - \frac{1}{3} \log[H_3PO_4]$$

$$\text{For } [H_3PO_4] = 0.01M, p[H]_{10^{-6}} = 8.72 - \frac{1}{12} pK_{sp} - \frac{1}{3} \log(10^{-2}) = 9.38 - \frac{1}{12} pK_{sp}$$

$$\text{For } [H_3PO_4] = 0.10M, p[H]_{10^{-6}} = 8.72 - \frac{1}{12} pK_{sp} - \frac{1}{3} \log(10^{-1}) = 9.05 - \frac{1}{12} pK_{sp}$$

For $Zr_3(PO_4)_4$, $K_{sp} = 1 \times 10^{-132}$, i.e., $pK_{sp} = 132$ at $25^\circ C$

$\therefore$ For $[H_3PO_4] = 0.01M$,

$$p[H]_{10^{-6}} = 9.38 - \frac{1}{12} \times 132 = -1.62,$$

and for $[H_3PO_4] = 0.10M$,

$$p[H]_{10^{-6}} = 9.05 - \frac{1}{12} \times 132 = -1.95.$$

Although the negative $p[H]$ values are undefined, nevertheless, these values mean the solution is strongly acidic. That is, zirconium phosphate is precipitated in fairly acidic solution.

The above approximations represent only partial pictures of the solubility equilibria, since the precipitation of the metallic hydroxides and the basic salts have not been taken into consideration in the calculations of $p[H]_{10^{-6}}$. However, the results, although approximate, provide scope for designing experimental conditions for removal of the phosphate radical from the solution before proceeding to perform the tests for cation radicals in neutral and ammoniacal medium. As for example, if the $p[H]$ of the test solution containing phosphate radical is adjusted with a buffer solution of appropriate $p[H]$, the metallic phosphates whose solubility products are exceeded with the prevailing phosphate ion concentration at this $p[H]$, are precipitated, if such metal ions are present in the test solution. The remaining phosphates, if any, may be removed by addition a suitable metal ion solution adjusted to the proper $p[H]$. In systematic group analysis, the phosphate removal is carried out following this principle.

If the test solution containing phosphate is rendered ammoniacal with NH_4Cl and $aq - NH_3$ after precipitation of Group-II metals as sulfides and removal of H_2S thereafter, phosphates of metals of Groups IIIA to Group-V (Mg^{2+}) along with some of their hydroxides and basic salts are precipitated all together. But if $p[H]$ of the solution is adjusted to 4 to 4.5 using acetic acid – acetate (1:1) buffer mixture, phosphates of only Group-IIIA metals, i.e. (Fe^{III} , Al^{III} , Cr^{III}) along with some of their hydroxides and basic salts are precipitated, keeping the metal ions of the following Groups in solution.

To remove the remaining phosphate from the solution, a suitable metal ion solution, adjusted to proper $p[H]$, such as "*neutral $FeCl_3$ solution*", is added in slight excess and the solution is warmed to facilitate the formation and coagulation of Fe^{III} phosphate precipitate. After removal of the phosphate precipitate by filtration, the excess Fe^{3+} ion is removed from the filtrate by precipitating as $Fe(OH)_3$, on treatment with NH_4Cl and aqueous ammonia solution. Only brown precipitate of $Fe(OH)_3$ appears at this stage, the metals of Group-IIIB to V (Mg^{2+}) remain in solution, as phosphate has been removed. Separation of Group-IIIB, IV and V metals may now be carried out by the usual procedures.

Note: Calculation of $p[H]$ of precipitation of metal hydroxides (of problem 2.5) using their solubility products from Appendix-A4 will reveal that for majority of the metals (other than alkali metals) phosphate precipitates are always contaminated with hydroxide precipitates. As for example, pH of precipitation of $FePO_4$ from $0.01M Fe^{3+}$ solution in presence of $0.01M H_3PO_4$ is 2.59 (of example 2.22 (ii)), whereas, pH of precipitation of $Fe(OH)_3$ from $0.01M Fe^{3+}$ solution is ~ 3 . Therefore, if pH of the solution is greater than 3, both phosphate and hydroxide will precipitate simultaneously.

2.3 Complex Equilibria

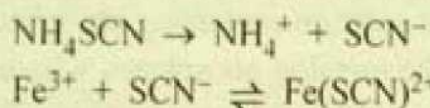
(a) Stability of Complexes in Solution: Stability Constants

The term *complex* or, *coordination complex* in inorganic chemistry means an association or assembly of atoms/ions/molecules, in which a metal ion at the center is bonded to a definite

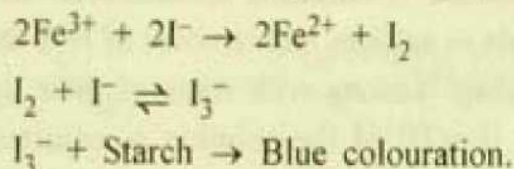
number of small molecules or ions such as NH_3 , Cl^- , OH^- , CN^- , SCN^- etc. called *ligands*, forming a new entity of definite geometry in such a manner that the properties of the individual components are lost and new properties, characteristic of the assembly are exhibited.

Examples. (2.23)

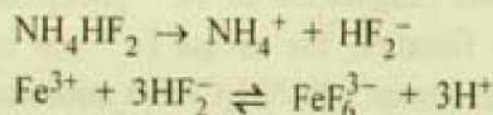
- (1) When a colourless solution of ammonium thiocyanate (NH_4SCN) is added to a colourless solution of ferric nitrate in dilute nitric acid, an intense blood red colouration is produced due to the formation of the complex, $\text{Fe}(\text{SCN})^{2+}$ ion.



- (2) If a drop of starch-potassium iodide solution is added to a solution of ferric chloride in dilute hydrochloric acid, an intense blue colouration appears, as Fe^{3+} oxidizes I^- ion to free iodine molecules (I_2), which react with excess iodide to form the complex, triiodide ion, I_3^- , that forms a blue adsorption complex with starch solution.

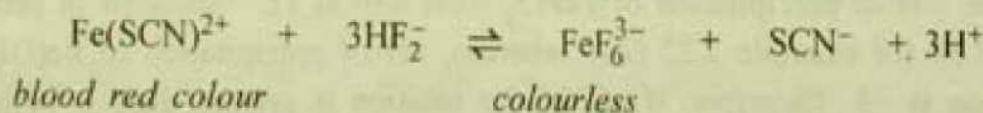


On the other hand, if the ferric chloride solution is first treated with an excess of ammonium bifluoride (NH_4HF_2) solution and then a drop of starch-potassium iodide solution is added, blue colouration is not produced, as Fe^{3+} ion reacts with F^- ion to form the complex, FeF_6^{3-} ion. As a result of that, Fe^{3+} ion is rendered unreactive to starch-potassium iodide solution.



This is an example which shows how the property of a metal ion is changed due to complex formation.

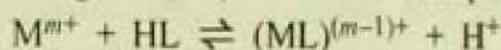
- (3) If to the blood red coloured solution containing the complex $\text{Fe}(\text{SCN})^{2+}$ ion (Example - 1) is added drops of concentrated aqueous solution of ammonium bifluoride, the blood red colour is discharged, as F^- ion displaces the SCN^- ion from the $\text{Fe}(\text{SCN})^{2+}$ complex, eventually producing the colourless complex FeF_6^{3-} ion.



This displacement reaction (Example-3) is just a manifestation of *HSAB principle*. Fe^{3+} ion is a *hard Lewis acid* and F^- ion is a *hard Lewis base*, whereas, SCN^- ion is a *soft or borderline Lewis base*. Naturally the hard-hard combination, i.e., the FeF_6^{3-} complex is more stable than the hard-soft combination, i.e., the $\text{Fe}(\text{SCN})^{2+}$ complex. Knowledge of *stability constants* of complexes are extremely helpful in predicting the directions of such complex

formation/dissociation/displacement reactions involving a metal ion, forming complexes with more than one type of ligands simultaneously.

Stability of a complex may be expressed in thermodynamic sense as well as in kinetic sense. *Kinetic stability* of a complex is a measure of the slowness with which the complex attains equilibrium with its constituents and may be expressed by the rates of such reactions of the complex. Kinetically stable complexes are also called *inert complexes*. Among the common metal ions, kinetically inert complexes are formed by the two first row transition metal ions, $\text{Cr}^{3+}(\text{d}^3)$ and $\text{Co}^{3+}(\text{d}^6)$. On the other hand, the reactions of the remaining 3d- transition series metal ions, eg., Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} ; (4d-series) Ag^+ and Cd^{2+} (5d-series) Hg_2^{2+} , Hg^{2+} ; alkali and alkaline earth (s-block) metal ions, Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} and p-block metal ions, Al^{3+} , Sn^{2+} , Pb^{2+} , Bi^{3+} etc. are very rapid and equilibria are attained almost instantaneously. Complexes of these rapidly reacting metal ions are called *labile complexes*. Stability of labile complexes are expressed by their *thermodynamic stability constants*, which is the activity quotient of the complex formation equilibria. If a metal ion (M^{m+}) reacts with a ligand (HL) to form a complex $(\text{ML})^{(m-1)+}$, according to,



then, applying the *law of mass action* at equilibrium, the activity (*a*'s) quotient or the thermodynamic stability constant (K°) of the complex $(\text{ML})^{(m-1)+}$ is defined as,

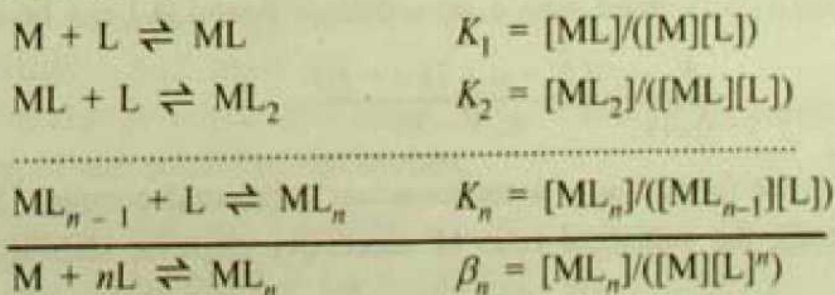
$$K^\circ = \frac{a_{(\text{ML})^{(m-1)+}}}{a_{\text{M}^{m+}} a_{\text{L}^-}}$$

For complex formation equilibria in dilute solution, for which activity coefficients (*f*'s) are close to unity, and so activities ($a = c.f$) of the species may be replaced by respective concentrations, and it is useful for all practical purposes, to define *stoichiometric stability constants* (*K*), which is the concentration quotient of the complex formation equilibrium,

$$K = \frac{[(\text{ML})^{(m-1)+}]}{[\text{M}^{m+}][\text{L}^-]}$$

Stepwise and overall stability constants

Complex formation reactions take place in stepwise manner. If a metal ion (M) reacts with a ligand (L) in dilute solution, to form a series of mononuclear complexes ML , ML_2 , ML_3 ... ML_n , then the stepwise stoichiometric stability constants (K_n , $n = 1, 2, 3 \dots n$) of the successive complexes, ML , ML_2 , ... ML_{n-1} , ML_n and the overall stability constant (β_n) of the complex ML_n may be defined according to:



As the overall reaction is the summation of all the stepwise reactions, the overall *formation constant* (β_n) is the product of all the stepwise formation constants:

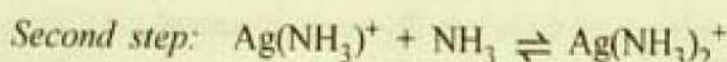
$$\beta_n = K_1 \times K_2 \times \dots \times K_{n-1} \times K_n$$

Example: (2.24)

For Ag^+ ammine complex formation, the stepwise and overall stability constants may be defined as,



$$K_1 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} = 2.1 \times 10^3 \quad (25^\circ \text{C})$$



$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} = 8.1 \times 10^3 \quad (25^\circ \text{C})$$

The overall reaction:



The overall stability constant, β_2 may be expressed as,

$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} \times \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$\therefore \beta_2 = K_1 \cdot K_2 = 2.1 \times 10^3 \times 8.1 \times 10^3 = 1.7 \times 10^7$$

In the absence of any valency interaction of ionic, covalent or π -bonding types between the successive steps of complex formation, the successive stability constants (K_n , $n = 1, 2, \dots, n \dots N$) of a series of mononuclear complexes, ML , $\text{ML}_2 \dots \text{ML}_n \dots \text{ML}_{N-1}$, ML_N , tend to decrease in magnitude due to statistical factors:

$$K_1 > K_2 > \dots > K_n > K_{n+1} \dots K_{N-1} > K_N$$

As the metal ion binds the ligands one after another, number of available coordination sites around the metal ion are successively reduced, thereby the probability of formation of successive complexes are progressively lowered. For a metal ion of coordination number, N , the statistical ratio of successive stability constants, K_n and K_{n+1} , of the mononuclear complexes ML_n and ML_{n+1} respectively, formed with a monodentate ligand (L) can be expressed by the relation:

$$\frac{K_n}{K_{n+1}} = \frac{(N - n + 1)(n + 1)}{n(N - n)}$$

Thus, for the formation of a mononuclear octahedral complex, ML_6 (where, L is a monodentate ligand), the statistical ratio of successive stepwise stability constants should be:



$$K_1 : K_2 : K_3 : K_4 : K_5 : K_6$$

$$\frac{6}{1} : \frac{5}{2} : \frac{4}{3} : \frac{3}{4} : \frac{2}{5} : \frac{1}{6}$$

Similarly for the association of three molecules of a symmetrical bidentate ligand (LL) such as ethylenediamine, to form an octahedral complex, $M(LL)_3$, the statistical ratio of the successive stepwise stability constants should be :

$$K_1 : K_2 : K_3 = \frac{12}{1} : \frac{5}{2} : \frac{4}{15}$$

Similarly, it can also be shown that for the formation of a square planar or a tetrahedral complex, $M(LL)_2$, with a symmetrical bidentate ligand (LL), the statistical ratio of the successive stability constants, $K_1 : K_2$ should be equal to $(2/1) : (1/2)$.

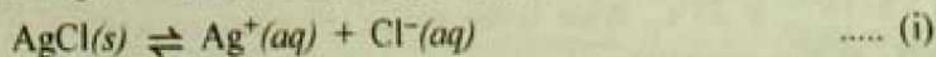
However, in real complexes, ratios of the successive stability constants differ from their statistical values, since the chemical, electrical, stereochemical and steric factors influence the magnitude of the stability constants.

The thermodynamic stability constant (K°) of the complex is a constant at a particular temperature. Its magnitude does not depend upon the detail composition of the solution or upon the presence or absence of other ions in the solution. It is, however, a theoretical constant, useful for interpreting the reactions. It is valid only at *infinite dilution*, i.e. at zero ionic strength, hence, it is symbolized as K° . Stoichiometric stability constant (K) is actually the *practical constant*, which depends, upon temperature as well as upon the detail composition of the solution. Knowledge of stoichiometric stability constants are extremely useful in predicting the directions of composite chemical reactions, designing preparative and separation procedures and testing the quantitateness of complex formation reactions. Redox properties of metal ions are greatly influenced when the metal ion forms complexes with a ligand (e.g. reaction of Fe^{3+} with I^- in presence of F^- , c.f. example-2.23(2) and Sect. 2.4).

(b) Effect of Complex Formation on Solubility

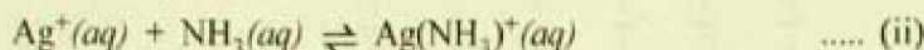
Solubility of sparingly soluble ionic compounds of metals increase dramatically in presence of Lewis bases (i.e. ligands) that can form coordinate covalent bonds with the metal cations. A common example of this kind of property is the dissolution of solid silver chloride, $AgCl(s)$, in aqueous ammonia. In the detection of chloride radical, when the test solution, acidified with nitric acid, is treated with silver nitrate ($AgNO_3$) solution, curdy white precipitate of $AgCl(s)$ appears, which shows $AgCl$ is sparingly soluble in water and in acid. If the precipitated $AgCl$ is treated with dilute aqueous ammonia solution, the precipitate passes into solution, forming the complex, diamminesilver(I), $Ag(NH_3)_2^+$ ion. The precipitate of $AgCl$ reappears if ammonia is neutralized by acidification with nitric acid.

According to *Le Chatelier principle*, dissolution of $AgCl$ in aqueous ammonia solution is the outcome of shifting of the solubility equilibrium,

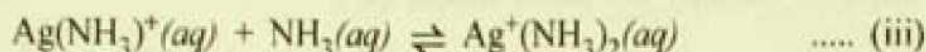


$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10} \text{ (25}^\circ\text{C)}$$

to the right due to tying up of the $\text{Ag}^+(\text{aq})$ ions in the form of the complex, $\text{Ag}(\text{NH}_3)_2^+$ ion, in stepwise manner according to,



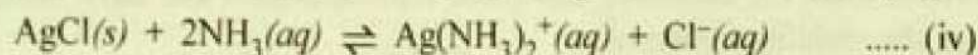
$$K_1 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} = 2.1 \times 10^3 \quad (25^\circ \text{C})$$



$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} = 8.1 \times 10^3 \quad (25^\circ \text{C})$$

where, K_{sp} is the solubility product of $\text{AgCl}(s)$ and K_1 and K_2 are the first and second step stability constants of the complex, $\text{Ag}(\text{NH}_3)_2^+$ ion.

Summing up the reactions (i), (ii) and (iii), we get the net reaction (iv),



$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$

The overall equilibrium constant, K , of the net reaction is the product of the equilibrium constants of the three step reactions (i), (ii) and (iii).

$$K_{sp} \cdot K_1 \cdot K_2 = [\text{Ag}^+][\text{Cl}^-] \times \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} \times \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]}$$

$$= \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = K$$

$$\therefore K = K_{sp} \cdot K_1 \cdot K_2$$

$$= (1.8 \times 10^{-10}) \cdot (2.1 \times 10^3) \cdot (8.1 \times 10^3) = 3.06 \times 10^{-3}$$

$$\therefore K \gg K_{sp}$$

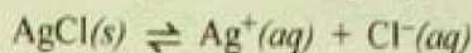
Since the magnitude of the equilibrium constant (K) of the overall reaction (iv) is much higher than the solubility product (K_{sp}), the solubility equilibrium (i) of AgCl in presence of ammonia shifts to the right.

Solubility of sparingly soluble ionic compounds of metals in general increase due to complex formation of the metal ions with suitable ligands in equilibrium with the precipitate.

Example (2.25)

Overall stability constant of the complex ion, $\text{Ag}(\text{NH}_3)_2^+$ is 1.7×10^7 and solubility product of AgCl is 1.8×10^{-10} at 25°C . What is the molar solubility of AgCl in (i) pure water and in (ii) 3 (M)NH_3 at this temperature?

- (i) Molar solubility of AgCl in pure water is the equilibrium concentration of Ag^+ ion in a saturated solution of AgCl. Solubility equilibrium of $\text{AgCl}(s)$ is,



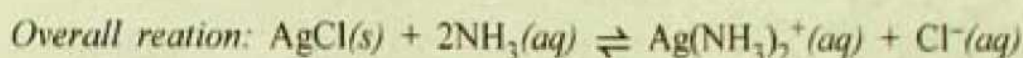
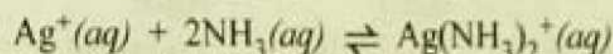
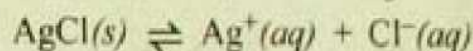
$$\therefore [\text{Ag}^+] = [\text{Cl}^-]$$

$\therefore$ Solubility product of $\text{AgCl}(s)$ is,

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+]^2 = 1.8 \times 10^{-10}$$

$$\therefore [\text{Ag}^+] = \sqrt{1.8 \times 10^{-10}} = 1.34 \times 10^{-5} (M)$$

- (ii) Dissolution of $\text{AgCl}(s)$ in aqueous NH_3 takes place according to the following steps:



Equilibrium constant (K) of the overall reaction is,

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2}$$

$\therefore$ Solubility product of $\text{AgCl}(s)$, $K_{sp} = [\text{Ag}^+][\text{Cl}^-]$

$$\therefore [\text{Cl}^-] = \frac{K_{sp}}{[\text{Ag}^+]}$$

Overall stability constant β_2 of $\text{Ag}(\text{NH}_3)_2^+$ is,

$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2}$$

$$\therefore [\text{Ag}(\text{NH}_3)_2^+] = \beta_2[\text{Ag}^+][\text{NH}_3]^2$$

Substituting for $[\text{Cl}^-]$ and $[\text{Ag}(\text{NH}_3)_2^+]$ in the expression for K , one obtains.

$$K = \frac{\beta_2[\text{Ag}^+][\text{NH}_3]^2}{[\text{NH}_3]^2} \times \frac{K_{sp}}{[\text{Ag}^+]}$$

$$\therefore K = \beta_2 K_{sp} = 1.7 \times 10^7 \times 1.8 \times 10^{-10} = 3.06 \times 10^{-3}$$

If x be the number of moles.lit⁻¹ of $\text{AgCl}(s)$ dissolves in 3(M) aqueous NH_3 , then at equilibrium, saturated solution of AgCl in aqueous NH_3 contains x mol.lit⁻¹ of $\text{Ag}(\text{NH}_3)_2^+$, x mol.lit⁻¹ of Cl^- and $(3 - 2x)$ mol.lit⁻¹ of NH_3 , assuming $\text{Ag}(\text{NH}_3)_2^+$ is the only silver containing species in the ammoniacal solution, i.e. all the $\text{Ag}^+(aq)$ produced in the solubility equilibrium are transformed into the complex $\text{Ag}(\text{NH}_3)_2^+$ ion, in presence of such a large excess of NH_3 . Therefore,

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{(x)(x)}{(3-2x)^2} = 3.06 \times 10^{-3}$$

$$\therefore x = 0.15 \text{ mol.lit}^{-1}$$

Thus, molar solubility of $\text{AgCl}(s)$ increases from $1.34 \times 10^{-5} \text{ mol.lit}^{-1}$ in pure water to $0.15 \text{ mol.lit}^{-1}$ in 3 mol.lit^{-1} of aqueous NH_3 solution.

Silver bromide AgBr ($K_{sp} = 5.4 \times 10^{-13}$ at 25°C) and silver iodide, AgI ($K_{sp} = 8.5 \times 10^{-17}$ at 25°C) are much less soluble than silver chloride. Following similar procedure, solubilities of AgBr and AgI in water and in $3(M)$ aqueous ammonia may be calculated and compared with those of AgCl ;

	AgCl	AgBr	AgI
Solubility product K_{sp} (25°C)	1.8×10^{-10}	5.4×10^{-13}	8.5×10^{-17}
Solubility in water (mol.lit^{-1})	1.34×10^{-5}	7.35×10^{-7}	9.22×10^{-9}
Solubility in $3(M)$ NH_3 (mol.lit^{-1})	0.15	9.04×10^{-3}	1.05×10^{-4}

Since the overall stability constant (β_2) of the complex $\text{Ag}(\text{NH}_3)_2^+$ ion is quite large,

$$\beta_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = 1.7 \times 10^7 \text{ (at } 25^\circ\text{C)}$$

whatever small amount of Ag^+ ion is produced by the solubility equilibrium, it is transformed into this complex, of which the concentration is directly proportional to the square of the concentration of ammonia.

Although solubility of all the silver halides (AgCl , AgBr , AgI) are increased in presence of $3(M)$ aq NH_3 solution, only the solubility of $\text{AgCl}(s)$ is considerable, and on acidification with HNO_3 the precipitate of AgCl reappears. For dissolution of AgBr to a detectable extent, much higher concentration of ammonia is required. In qualitative inorganic analysis for the detection of Cl^- , Br^- and I^- by AgNO_3 test, it is found that the precipitate of AgCl dissolves even in dilute aqueous - NH_3 or in ammonium carbonate solution, AgBr dissolves in concentrated (liquor) NH_3 , whereas, AgI remains undissolved even in concentrated NH_3 , (cf, Sect. 5.11-5.13).

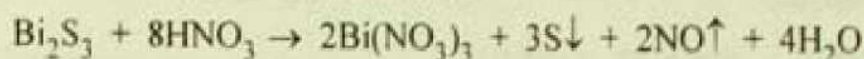
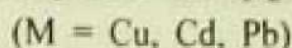
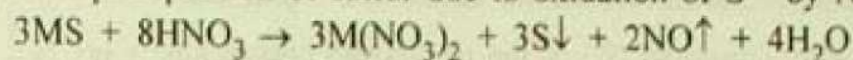
Problems (2.8)

- (1) What happens when KBr solution is added to a dilute ammoniacal solution of AgCl ? Give equations.
- (2) What happens when KI solution is added to a concentrated ammoniacal solutions of (i) AgCl , and (ii) AgBr ? Give equations.

Another well known example of the influence of complex formation on precipitation is the detection of Cd^{2+} in presence of Cu^{2+} by precipitation of sulfide in the systematic group separation of Group-IIA metal sulfides (cf. Sect. 7.8).

When a mixture of Group - IIA metal sulfides (HgS , PbS , Bi_2S_3 , CuS and CdS) is treated

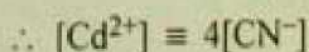
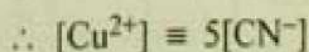
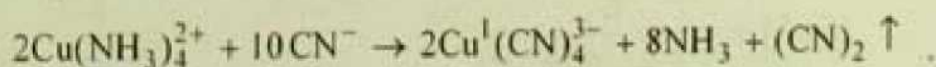
with hot dilute HNO_3 , mercuric sulfide (HgS) remains undissolved, the remaining sulfides dissolve in HNO_3 with precipitation of sulfur due to oxidation of S^{2-} by NO_3^- according to,



The resulting solution after separation of sulfur by filtration, contains Pb^{2+} , Cu^{2+} , Cd^{2+} and Bi^{3+} (or, BiO^+) in the form of their nitrate salts. When this solution is rendered strongly ammoniacal, Pb^{2+} and Bi^{3+} precipitate as their hydroxides or hydrous oxides, $\text{Pb}(\text{OH})_2$ and $\text{Bi}(\text{OH})_3$ (or $\text{BiO}(\text{OH})$) respectively, whereas, Cu^{2+} and Cd^{2+} remain in ammoniacal solution as their ammine complexes, $\text{Cu}(\text{NH}_3)_4^{2+}$ (deep blue) and $\text{Cd}(\text{NH}_3)_4^{2+}$ (colourless). Blue colouration of this ammoniacal solution indicates the presence of Cu^{2+} . In absence of Cu^{2+} , the ammoniacal solution is colourless. If Cd^{2+} is present, yellow precipitate of CdS appears on treatment of this solution with H_2S -water. But if the solution is blue, i.e. if Cu^{2+} is present, addition of H_2S -water produces a black precipitate, due CuS . If Cd^{2+} is also present, yellow precipitate of CdS is formed, but its yellow colour is masked by the black colour of CuS . That is, in presence of Cu^{2+} , it is difficult to detect Cd^{2+} by sulfide precipitation.

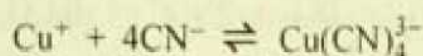
However, the problem may be overcome by several ways. The most convenient and easiest way is to carry out selective precipitation by controlling S^{2-} ion concentration through adjustment of H^+ ion concentration of the solution or by capillary separation technique (*cf. p-57*). Another, very interesting method of detection of Cd^{2+} in presence of Cu^{2+} is based on the application of complex formation of these metals ions with cyanide (CN^-) ion in ammoniacal medium, followed by treatment with H_2S - water, when only the yellow precipitate of CdS appears, whereas, copper is rendered unreactive to S^{2-} ion due the formation of very stable cyano complex, $[\text{Cu}^{\text{I}}(\text{CN})_4]^{3-}$ ion.

When the deep blue ammoniacal solution, containing the complexes $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Cd}(\text{NH}_3)_4^{2+}$ ions, is treated with an excess of potassium cyanide (KCN) solution (**CAUTION.POISON**), the blue colour of the test solution is discharged as Cu^{II} in the ammine complex, $\text{Cu}(\text{NH}_3)_4^{2+}$ ion, is reduced to Cu^{I} which is complexed as $[\text{Cu}^{\text{I}}(\text{CN})_4]^{3-}$ ion by the CN^- ions. The Cd^{II} -cyano complex, $[\text{Cd}(\text{CN})_4]^{2-}$ is also formed replacing the NH_3 ligands from the $\text{Cd}(\text{NH}_3)_4^{2+}$ complex by the CN^- ions:



Since CN^- ion is a *soft Lewis base* ligand, it form more stable complex with the *soft Lewis acid*, Cu^+ , than with the *borderline Lewis acids*, Cu^{2+} and Cd^{2+} .

The overall stability constants (β) of the tetracyano complexes, $\text{Cu}(\text{CN})_4^{3-}$ and $\text{Cd}(\text{CN})_4^{2-}$ ions may be defined as,



$$\beta_{\text{Cu}} = \frac{[\text{Cu}(\text{CN})_4^{3-}]}{[\text{Cu}^+][\text{CN}^-]^4} = 2 \times 10^{30} \quad (\text{at } 25^\circ \text{C})$$



$$\beta_{\text{Cd}} = \frac{[\text{Cd}(\text{CN})_4^{2-}]}{[\text{Cd}^{2+}][\text{CN}^-]^4} = 1.29 \times 10^{17} \quad (\text{at } 25^\circ \text{C})$$

As the overall stability constants (β) are inversely related to the equilibrium concentrations of the free metal ions (Cu^+ and Cd^{2+}), the higher is the value of β , the lower is the concentration of the free metal ion available to react with other reagents, such as S^{2-} ion, when H_2S - water is added.

In presence of a large excess of CN^- ion, assuming that, the $\text{Cu}(\text{CN})_4^{3-}$ and $\text{Cd}(\text{CN})_4^{2-}$ ions are the only complexed forms of these two metal ions and the free metal ions exist only as Cu^+ and Cd^{2+} respectively, the mass balance equations for the two metal ions, neglecting the concentrations of the ammine complexes for simplicity, become,

$$T_{\text{Cu}} = [\text{Cu}^+] + [\text{Cu}(\text{CN})_4^{3-}]$$

$$T_{\text{Cd}} = [\text{Cd}^{2+}] + [\text{Cd}(\text{CN})_4^{2-}]$$

where, T_{Cu} and T_{Cd} are the total concentrations of Cu^{2+} and Cd^{2+} respectively in the solution. Equilibrium concentrations of the complexed metal ions are, given by :

$$[\text{Cu}(\text{CN})_4^{3-}] = \beta_{\text{Cu}}[\text{Cu}^+][\text{CN}^-]^4$$

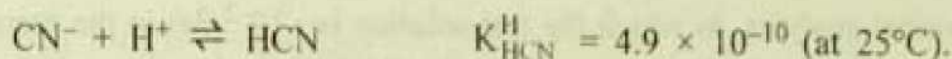
$$[\text{Cd}(\text{CN})_4^{2-}] = \beta_{\text{Cd}}[\text{Cd}^{2+}][\text{CN}^-]^4$$

Substituting for these terms in the mass balance equations for the two metal ions, it will be seen that the equilibrium concentrations of the free Cu^+ and Cd^{2+} ions are inversely related to the fourth power of cyanide ion concentration:

$$[\text{Cu}^+] = \frac{T_{\text{Cu}}}{1 + \beta_{\text{Cu}}[\text{CN}^-]^4}$$

$$[\text{Cd}^{2+}] = \frac{T_{\text{Cd}}}{1 + \beta_{\text{Cd}}[\text{CN}^-]^4}$$

Since CN^- ion is the conjugate base of a weak acid (HCN), it is a strong base and it has a profound affinity to bind a proton (H^+) to form the unionized HCN molecules according to,



Therefore, the concentration of CN^- ion in the solution will be governed by $p[\text{H}]$ of the test solution. Since the test solution containing the complexes, $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Cd}(\text{NH}_3)_4^{2+}$ and also $\text{Cu}(\text{CN})_4^{3-}$ and $\text{Cd}(\text{CN})_4^{2-}$ ions is strongly ammoniacal, the $p[\text{H}]$ of the solution is fairly high. For example, if the concentration of NH_3 in the test solution is modestly 1(M), then the $p[\text{H}]$ of the solution will be,

$$\begin{aligned} p[\text{H}] &= \frac{1}{2} pK_w + \frac{1}{2} pK_{\text{NH}_4} + \frac{1}{2} \log[\text{NH}_3] \\ &= \frac{1}{2} (14) + \frac{1}{2} (9.26) + \frac{1}{2} \log(1.0) \\ &= 7 + 4.63 = 11.63 \end{aligned}$$

At such a high $p[\text{H}]$, (11.63), major amount of the cyanide ligand will exist in the form of CN^- ion and only a very small fraction of it will exist in the form of unionized HCN molecules ($pK_{\text{HCN}}^{\text{H}}$ 9.31).

If T_{CN} be the total concentration of KCN (completely ionized salt) in the solution, then the mass balance equation of cyanide will be,

$$T_{\text{CN}} = [\text{HCN}] + [\text{CN}^-] + 4T_{\text{Cu}} + 4T_{\text{Cd}}$$

HCN ionizes as a weak acid according to,



$$K_{\text{HCN}}^{\text{H}} = \frac{[\text{H}^+][\text{CN}^-]}{[\text{HCN}]}$$

$$\therefore [\text{HCN}] = \frac{[\text{H}^+]}{K_{\text{HCN}}^{\text{H}}} [\text{CN}^-]$$

$$\therefore T_{\text{CN}} = [\text{CN}^-] \left(\frac{[\text{H}^+]}{K_{\text{HCN}}^{\text{H}}} + 1 \right) + 4(T_{\text{Cu}} + T_{\text{Cd}})$$

$$\therefore [\text{CN}^-] = \frac{T_{\text{CN}} - 4(T_{\text{Cu}} + T_{\text{Cd}})}{\left(\frac{[\text{H}^+]}{K_{\text{HCN}}^{\text{H}}} + 1 \right)}$$

Using this equation, and knowing $K_{\text{HCN}}^{\text{H}}$ one may calculate the equilibrium concentration of CN^- ion in the solution containing known amount (T_{CN}) of KCN and known amounts (T_{Cu} , T_{Cd}) of the metal ions (i.e., Cu^+ , Cd^{2+} respectively) provided $T_{\text{CN}} \gg (T_{\text{Cu}} + T_{\text{Cd}})$.

For a typical analysis, in which the test solution is $\sim 10^{-2}(M)$ in the metal ions and $0.5(M)$ in KCN, and it is strongly ammoniacal suppose, $[\text{NH}_3] = 1(M)$, the equilibrium concentration of CN^- ion may be calculated using the above relation as follows:

$$T_{\text{CN}} = 0.5(M), T_{\text{Cu}} = 0.01(M), T_{\text{Cd}} = 0.01(M)$$

$$p[\text{H}] \text{ of } 1(M) \text{ NH}_3 \text{ solution} = 11.63 \text{ (calculated before).}$$

$$\frac{[\text{H}^+]}{K_{\text{HCN}}^{\text{H}}} = \text{Inverse log } (pK_{\text{HCN}}^{\text{H}} - p[\text{H}]) = \text{Inverse log } (9.31 - 11.63) = 4.79 \times 10^{-3}$$

$$\therefore \left(\frac{[\text{H}^+]}{K_{\text{HCN}}^{\text{H}}} + 1 \right) \text{ at } p[\text{H}] \text{ 11.63 is } = (4.79 \times 10^{-3} + 1) \approx 1.0048$$

$$\therefore [\text{CN}^-] = \frac{0.5 - 4(0.01 + 0.01)}{1.0048}(M) \approx 0.418 M$$

More over, one equivalent of CN^- ion is consumed in reducing Cu^{2+} to Cu^+ . Therefore, the actual equilibrium concentration of free CN^- ion will be equal to $(0.418 - 0.01) = 0.408M \approx 0.41(M)$.

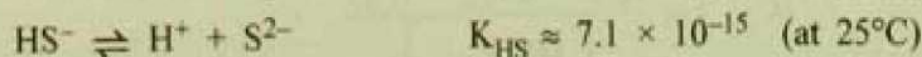
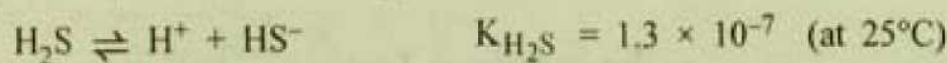
Therefore, the equilibrium concentrations of free Cu^+ and free Cd^{2+} ions under this $[\text{CN}^-]$ ion concentration will be :

$$[\text{Cu}^+] = \frac{T_{\text{Cu}}}{1 + \beta_{\text{Cu}}[\text{CN}^-]^4} = \frac{0.01}{1 + (2 \times 10^{30}) \times (0.41)^4} = 1.77 \times 10^{-31}(M)$$

$$[\text{Cd}^{2+}] = \frac{T_{\text{Cd}}}{1 + \beta_{\text{Cd}}[\text{CN}^-]^4} = \frac{0.01}{1 + (1.29 \times 10^{17})} = 2.74 \times 10^{-18}(M)$$

Therefore, $[\text{Cu}^+] \ll [\text{Cd}^{2+}]$.

Let us now examine, what happens when this ammoniacal mixture of $\text{Cu}(\text{CN})_4^{3-}$ and $\text{Cd}(\text{CN})_4^{2-}$ ions, is treated with H_2S -water. Saturated solution of H_2S at 25°C and 1 atm. pressure is $\sim 0.1(M)$ in H_2S . In aqueous solution H_2S ionizes as a weak diprotic acid according to,



Since the $p[\text{H}]$ of the ammoniacal test solution will be > 11.5 , H_2S in this solution will

be completely converted to HS^- ion, which at this $p[\text{H}]$ will only partially deprotonate to produce the sulfide (S^{2-}) ion. Since the total concentration of $[\text{H}_2\text{S}] = 0.1(M)$ in its saturated solution, therefore, at $p[\text{H}] \geq 11.5$, the mass balance equation for H_2S will be,

$$[\text{HS}^-] + [\text{S}^{2-}] = 0.1(M)$$

Since the $p[\text{H}]$ of the ammoniacal solution ($[\text{NH}_3] = 1(M)$) is 11.63) therefore, the ratio of $[\text{S}^{2-}]/[\text{HS}^-]$ in this solution may be calculated applying *Handerson-Hasselbalch equation* using the second ionisation constant (K_{HS}) of H_2S ,

$$p[\text{H}] = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$p[\text{H}] = pK_{\text{HS}} + \log \frac{[\text{S}^{2-}]}{[\text{HS}^-]}$$

$$11.63 \approx 14.15 + \log \frac{[\text{S}^{2-}]}{[\text{HS}^-]}$$

(where, $pK_{\text{HS}} = -\log K_{\text{HS}} \approx -\log(7.1 \times 10^{-15}) = 14.15$), which gives,

$$\frac{[\text{S}^{2-}]}{[\text{HS}^-]} \approx 0.003$$

$$\therefore [\text{HS}^-] \approx \frac{[\text{S}^{2-}]}{0.003}$$

From the mass balance equation of H_2S at this $p[\text{H}]$, we get,

$$[\text{HS}^-] + [\text{S}^{2-}] = 0.1 (M)$$

$$\therefore \frac{[\text{S}^{2-}]}{0.003} + [\text{S}^{2-}] = 0.1 (M)$$

which gives, $[\text{S}^{2-}] \approx 3 \times 10^{-4}(M)$.

Solubility products of Cu_2S and CdS are given by,

$$(K_{\text{sp}})_{\text{Cu}_2\text{S}} = [\text{Cu}^+]^2[\text{S}^{2-}] = 2.5 \times 10^{-48} \text{ (at } 25^\circ \text{ C)}$$

$$(K_{\text{sp}})_{\text{CdS}} = [\text{Cd}^{2+}][\text{S}^{2-}] = 7.9 \times 10^{-27} \text{ (at } 25^\circ \text{ C)}$$

Now, substituting the values of $[\text{Cu}^+]$, $[\text{Cd}^{2+}]$ and $[\text{S}^{2-}]$ calculated above, one obtains,

$$\text{for } [\text{Cu}^+]^2 \times [\text{S}^{2-}] = (1.77 \times 10^{-31})^2 \times (3 \times 10^{-4})$$

$$= 9.4 \times 10^{-66} < (K_{\text{sp}})_{\text{Cu}_2\text{S}}$$

$$\text{for } [\text{Cd}^{2+}] \times [\text{S}^{2-}] = (2.74 \times 10^{-18}) \times (3 \times 10^{-4})$$

$$= 8.22 \times 10^{-22} > (K_{\text{sp}})_{\text{CdS}}$$

Since the product, $[\text{Cd}^{2+}] \times [\text{S}^{2-}]$, exceeds the solubility product of CdS , yellow precipitate of CdS appears on addition of H_2S - water to the test solution. On the other hand, the product $[\text{Cu}^+]^2 \times [\text{S}^{2-}]$ is much smaller than the solubility product of Cu_2S , so copper remains in solution as its tetracyano complex, $[\text{Cu}(\text{CN})_4]^{3-}$ and Cu_2S is not precipitated when H_2S is added to this test solution.

(c) Masking and Demasking Reactions

(i) Masking reactions

The term *masking* is often used by chemists to identify complex formation reactions in which metal complexes of such high stabilities are formed that the metal ions are rendered unreactive towards other reagents.

Examples (2.26)

In the previous section we have come across the following reactions:

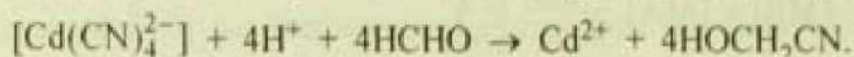
- (1) When a mixture of ammine complexes of Cu^{II} and Cd^{II} i.e. $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Cd}(\text{NH}_3)_4]^{2+}$ ions in Group - IIA analysis is treated with H_2S - water, both CuS (black) and CdS (yellow) are simultaneously precipitated. But only the black colour of CuS is visible, the yellow colour of CdS can not be visualized in presence of black CuS . But if the mixture of the two ammine complexes is first treated with an excess of KCN solution (**CAUTION: POISON**) and then H_2S - water is added, only yellow CdS is precipitated. Copper remains in solution in the form of its tetracyano complex, $[\text{Cu}^{\text{I}}(\text{CN})_4]^{3-}$, which is so highly stable ($\log \beta_4 = 30.3$) that copper is rendered unreactive to H_2S . Although Cd^{2+} also forms the tetracyano complex, $[\text{Cd}(\text{CN})_4]^{2-}$ ion, but its stability ($\log \beta_4 = 17.11$) is not as high as to render Cd^{2+} unreactive to H_2S . Although this method of detection of Cd^{2+} in presence of Cu^{2+} is not encouraged and has been practically abandoned due to poisonous nature of KCN , nevertheless, this offers a good example of masking reaction.
- (2) When an acid solution of Fe^{3+} is treated with NH_4SCN solution, a blood red colour is produced due to the formation of the complex, $\text{Fe}(\text{SCN})^{2+}$ ion. But in presence of a large excess of fluoride ion (NH_4HF_2 or NH_4F), the blood red coloured $\text{Fe}(\text{SCN})^{2+}$ complex can not be formed, as Fe^{3+} is masked by forming more stable complexes with fluoride ion ($\log K[\text{Fe}(\text{SCN})^{2+}] = 3.03$, $\log K[\text{FeF}_6^{3-}] = 6.04$).
- (3) When an aqueous solution of KI is added to a weakly acidic solution containing Fe^{3+} ion, a deep brown colour appears as Fe^{3+} ion oxidizes iodide ion (I^-) to liberate I_2 molecules, since $[E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77\text{V}] > [E^\circ(\text{I}_2/2\text{I}^-) = +0.54\text{V}]$. But if a few crystals of NH_4HF_2 is added to the solution of Fe^{3+} salt and then KI solution is added, iodine is not liberated and the solution remain colourless. This is because, Fe^{3+} ion is rendered unreactive to I^- due to the formation of fluoro complexes, (e.g. FeF_6^{3-} ion), as a result of which its *formal potential* (cf. Sect. 2.4) is decreased significantly.

(ii) Demasking reaction

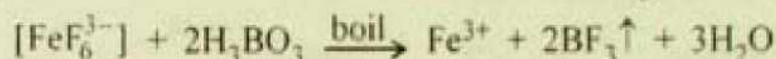
Demasking reactions are those reactions through which the metal ions are released from the otherwise unreactive metal-ligand complexes.

Examples (2.27)

- (1) A metal ion can be released from its cyano complex on treatment with formalin in dilute acidic solution: e.g, Cd^{2+} ion may be released from $[\text{Cd}(\text{CN})_4]^{2-}$ complex by this method,



- (2) Fe^{3+} ion may be released from its fluoro complexes by boiling the solution with boric and (H_3BO_3) , when fluoride is removed as volatile BF_3 ,



- (4) Both Ti(IV) and V (V) salts (rare elements) in dilute H_2SO_4 medium react with H_2O_2 to form coloured peroxo complexes.

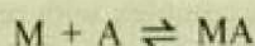
$\text{H}_2[\text{Ti}(\text{O}_2)(\text{SO}_4)_2]$ - peroxodisulfatotitanic acid - *Yellow colour.*

$\text{H}_3[\text{V}(\text{O}_2)\text{O}_3]$ - orthoperoxovanadic acid - *Wine red colour.*

On addition of a few crystals of NH_4HF_2 , the yellow colour of the Ti(IV) complex is discharged due to the formation hexafluoro complex of titanium, $[\text{TiF}_6]^{2-}$ ion. But when this colourless solution is gently warmed with small amount of H_3BO_3 , the yellow colour of the peroxo complex is restored, since fluoride ion is removed as volatile BF_3 .

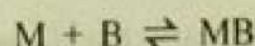
Oxovanadium (V) however does not form stable fluoro complexes. So the wine red colour of peroxo complex of V(V) is not discharged in presence of NH_4HF_2 . This of course also offers a means of detection of vanadium by this test even in presence of much titanium, by masking the latter as its fluoro complex.

Stability constants of the complexes play key roles in masking-demasking reactions. In the reaction of a metal ion (M) with a reagent (A) in presence of a masking agent (B), the metal ion is subjected to form complexes with two different ligands (A and B) simultaneously:



$$K_{\text{MA}} = \frac{[\text{MA}]}{[\text{M}][\text{A}]}$$

$$\therefore [\text{MA}] = K_{\text{MA}} \cdot [\text{M}][\text{A}]$$



$$K_{\text{MB}} = \frac{[\text{MB}]}{[\text{M}][\text{B}]}$$

$$\therefore [\text{MB}] = K_{\text{MB}} \cdot [\text{M}][\text{B}]$$

The relative proportion of the two complexes [MA] and [MB] depends upon the relative stabilities of these two complexes and also on the concentrations of the ligands A and B.

$$\frac{[MA]}{[MB]} = \frac{K_{MA} \cdot [M] \cdot [A]}{K_{MB} [M][B]} = \frac{K_{MA}}{K_{MB}} \cdot \frac{[A]}{[B]}$$

Concentration of the complex with the masking agent B is given by

$$[MB] = [MA] \cdot \frac{K_{MB}}{K_{MA}} \cdot \frac{[B]}{[A]}$$

Examples (2.28)

(1) Consider the two Fe^{III} complexes $\text{Fe}(\text{SCN})^{2+}$ and FeF^{2+} :

$$\log K_{\text{FeF}} = 6.04$$

$$\therefore K_{\text{FeF}} = 10^{6.04}$$

$$\log K_{\text{Fe}(\text{SCN})} = 3.03$$

$$\therefore K_{\text{Fe}(\text{SCN})} = 10^{3.03}$$

(charges are omitted for simplity)

$$[\text{FeF}] = [\text{Fe}(\text{SCN})] \times \frac{K_{\text{FeF}}}{K_{\text{Fe}(\text{SCN})}} \cdot \frac{[\text{F}^-]}{[\text{SCN}^-]}$$

$$= [\text{Fe}(\text{SCN})] \times \frac{10^{6.04}}{10^{3.03}} \times \frac{[\text{F}^-]}{[\text{SCN}^-]}$$

$$= [\text{Fe}(\text{SCN})] \cdot \frac{[\text{F}^-]}{[\text{SCN}^-]} \cdot 10^{3.01}$$

If the concentrations of the masking agent, F^- ion, and the reagent, SCN^- ion, are same, i.e., $[\text{F}^-] = [\text{SCN}^-]$, then,

$$[\text{FeF}] = [\text{Fe}(\text{SCN})] \times 10^{3.01} \approx [\text{Fe}(\text{SCN})] \times 1000.$$

As the Fe^{III} complex with the masking ligand (F^-) is ~1000 times more stable than the Fe^{III} complex with the reagent ligand (SCN^-), concentration of the complex with the masking ligand is ≈ 1000 times the concentration of the complex with reagent ligand, when the concentrations of the two ligands are same, since the stoichiometry of both the complexes are same i.e. (1:1). In presence of a large excess of F^- ligand, say $[\text{F}^-] = 10[\text{SCN}^-]$,

$$[\text{FeF}] = [\text{Fe}(\text{SCN})] \cdot 10 \cdot 10^{3.01} \approx [\text{Fe}(\text{SCN})] \times 10^4.$$

(2) Consider the complexes of Ni^{II} with CN^- ion and EDTA^{4-} ion. Complex formation of Ni^{2+} with CN^- and EDTA^{4-} ligands may be represented by the following equilibria,



$$K_{[\text{Ni}(\text{CN})_4]} = \frac{[\text{Ni}(\text{CN})_4]}{[\text{Ni}][\text{CN}]^4}$$

$$\therefore [\text{Ni}(\text{CN})_4^{2-}] = K_{[\text{Ni}(\text{CN})_4]} \cdot [\text{Ni}][\text{CN}]^4$$



$$K_{[\text{Ni}(\text{EDTA})]} = \frac{[\text{Ni}(\text{EDTA})]}{[\text{Ni}][\text{EDTA}]}$$

$$[\text{Ni}(\text{EDTA})] = K_{[\text{Ni}(\text{EDTA})]} \cdot [\text{Ni}][\text{EDTA}]$$

(Charges are omitted from the mathematical expressions for simplicity.)

$$\therefore \frac{[\text{Ni}(\text{CN})_4]}{[\text{Ni}(\text{EDTA})]} = \frac{K_{[\text{Ni}(\text{CN})_4]}}{K_{[\text{Ni}(\text{EDTA})]}} \cdot \frac{[\text{CN}]^4}{[\text{EDTA}]}$$

$$\therefore [\text{Ni}(\text{CN})_4] = [\text{Ni}(\text{EDTA})] \cdot \frac{K_{[\text{Ni}(\text{CN})_4]}}{K_{[\text{Ni}(\text{EDTA})]}} \cdot \frac{[\text{CN}]^4}{[\text{EDTA}]}$$

$$\text{At } 25^\circ\text{C, } \log K_{[\text{Ni}(\text{CN})_4]} = 31.3$$

$$\log K_{[\text{Ni}(\text{EDTA})]} = 18.6$$

$$\therefore [\text{Ni}(\text{CN})_4] = [\text{Ni}(\text{EDTA})] \frac{10^{31.3}}{10^{18.6}} \times \frac{[\text{CN}]^4}{[\text{EDTA}]}$$

$$= [\text{Ni}(\text{EDTA})] \times 10^{12.7} \times \frac{[\text{CN}]^4}{[\text{EDTA}]}$$

$$\text{If } [\text{CN}^-] = [\text{EDTA}] = 0.1 \text{ (M)}$$

$$\begin{aligned} [\text{Ni}(\text{CN})_4] &= [\text{Ni}(\text{EDTA})] \times 10^{12.7} \times \frac{(0.1)^4}{0.1} \\ &= [\text{Ni}(\text{EDTA})] \times 10^{9.7} \end{aligned}$$

$$\text{If } [\text{CN}^-] = 0.01 \text{ (M), } [\text{EDTA}] = 0.1 \text{ (M)}$$

$$\begin{aligned} [\text{Ni}(\text{CN})_4] &= [\text{Ni}(\text{EDTA})] \times 10^{12.7} \times \frac{(0.01)^4}{(0.1)} \\ &= [\text{Ni}(\text{EDTA})] \times 10^{5.7} \end{aligned}$$

It is evident from this discussion, that, CN^- ion forms complex of such high stability with Ni^{II} that even in presence of 10 fold excess of the EDTA^{4-} ligand, the concentration of the $[\text{Ni}(\text{CN})_4^{2-}]$ complex is almost 10^6 times the concentration of $[\text{Ni}(\text{EDTA})^{2-}]$ complex. Thus, CN^- ion renders Ni^{II} almost unreactive to EDTA^{4-} ligand, i.e., Ni^{II} is masked by CN^- ion.

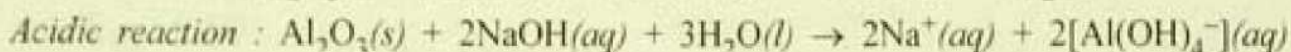
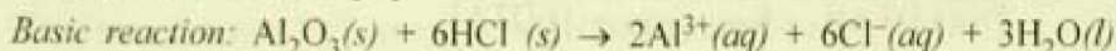
EDTA^{4-} is the fully deprotonated anion of ethylenediaminetetracetic acid (H_4EDTA), which is a hexadentate ligand, $(\text{HOOCCH}_2)_2\text{N} \cdot \text{CH}_2\text{CH}_2 \cdot \text{N}(\text{CH}_2\text{COOH})_2$.

(d) Amphoterism

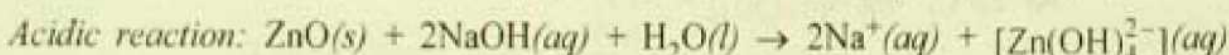
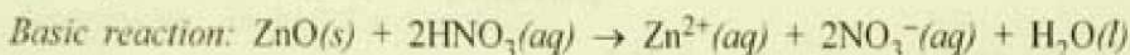
The term, *amphoterism*, comes from the Greek word "*amphoteris*" meaning "*in both ways*". Oxides and hydroxides of elements of intermediate electronegativities, have intermediate ionic and covalent characters in their bondings, and show both acidic and basic properties. As for example, Al_2O_3 , ZnO , PbO , SnO_2 etc. react with strong acids to form salts, with the metal ions as cations, and react with strong bases to form salts, in which these metals are present as salt anions.

Example (2.29)

(1) Amphoterism of Al_2O_3



(2) Amphoterism of ZnO

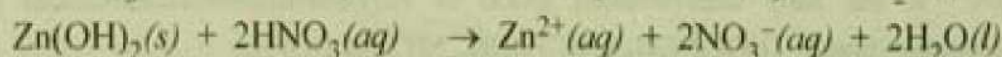
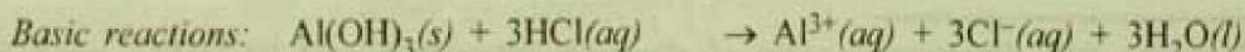


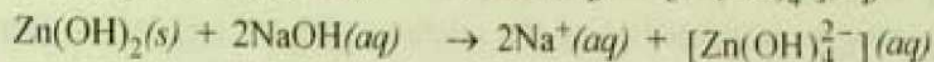
Acid-base character and ionic-covalent character of oxides depend upon the position of the oxide forming element in the periodic table and its oxidation number. Basic characters of oxides decrease and their acidic characters and covalent characters increase across the periodic table from the active metals on the left to the electronegative non-metals on the right. In the third period of the periodic table this variation is clearly demonstrated.

Periodic Groups						
1	2	13	14	15	16	17
Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl_2O_7
$\leftarrow \text{basic} \rightarrow$		amphoteric	.	$\leftarrow \text{acidic} \rightarrow$		

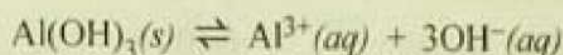
Basic character and ionic character of oxides increase downward from the more electronegative elements at the top of a periodic group to the less electronegative ones at the bottom. As for example in Group-15, N is at the top. Nitrogen oxides, N_2O_5 , NO_2 are strongly acidic, followed by phosphorus oxides, P_4O_{10} and P_4O_6 which are weakly acidic, arsenic and antimony oxides, As_2O_3 and Sb_2O_3 are amphoteric, whereas, bismuth oxide, Bi_2O_3 is basic. Thus, looking at the periodic table as a whole, we see the most acidic oxides occur at the upper right, the most basic oxides at the lower left and the amphoteric oxides in a roughly diagonal band stretching across the middle.

The hydroxides of the elements, forming amphoteric oxides, also show amphoteric behaviour. As for example, $\text{Al}(\text{OH})_3$ and $\text{Zn}(\text{OH})_2$ show amphotericism.



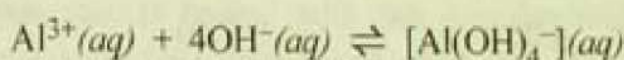


Dissolution of amphoteric oxides in alkali may be regarded as an example of the influence of complex formation on solubility. Since the dissolution of a hydroxide in alkali, involves complex formation with OH^- ion, solubility of the amphoteric hydroxides increase with rise of $p\text{H}$. Solubility of aluminium hydroxide at different $p\text{H}$ (Fig. 2.2) may be calculated from its solubility equilibrium.



$$K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3 = 1 \times 10^{-32} \text{ (at } 25^\circ\text{C)(i)}$$

The overall complex formation equilibrium of Al^{3+} with OH^- ions in dilute solution may be represented as,



$$\beta_4 = \frac{[\text{Al(OH)}_4^-]}{[\text{Al}^{3+}][\text{OH}^-]^4} = 3 \times 10^{33} \text{ (at } 25^\circ\text{C) (ii)}$$

Solubility of Al(OH)_3 at low $p[\text{H}]$ (i.e. in weakly acidic solution) is equal to the equilibrium concentration of $\text{Al}^{3+}(aq)$ ion, as given by the solubility equilibrium (i):

$$\begin{aligned} [\text{Al}^{3+}] &= \frac{K_{sp}}{[\text{OH}^-]^3} = \frac{K_{sp}}{(K_w / [\text{H}^+])^3} = \frac{K_{sp}[\text{H}^+]^3}{(K_w)^3} \\ &= \frac{10^{-32}[\text{H}^+]^3}{(10^{-14})^3} = 10^{10}[\text{H}^+]^3 \end{aligned}$$

On simplification and taking logarithm one may obtain,

$$p[\text{H}] = 3.33 - \frac{1}{3} \log[\text{Al}^{3+}] \quad \dots \text{ (iii)}$$

On the other hand, solubility of Al(OH)_3 at high $p[\text{H}]$ (i.e. in weakly alkaline solution) is equal to the equilibrium concentration of the complex $[\text{Al(OH)}_4^-](aq)$ ion, as given by the complex formation equilibrium (ii) as well as the solubility equilibrium (i):

$$\begin{aligned} \beta_4 &= \frac{[\text{Al(OH)}_4^-]}{[\text{Al}^{3+}][\text{OH}^-]^4} = \frac{[\text{Al(OH)}_4^-]}{[\text{Al}^{3+}][\text{OH}^-]^3 \times (K_w / [\text{H}^+])} = \frac{[\text{Al(OH)}_4^-][\text{H}^+]}{K_{sp} \cdot K_w} \\ \therefore [\text{Al(OH)}_4^-] &= \frac{\beta_4 \cdot K_{sp} \cdot K_w}{[\text{H}^+]} = \frac{3 \times 10^{33} \times 10^{-32} \times 10^{-14}}{[\text{H}^+]} = \frac{3 \times 10^{-13}}{[\text{H}^+]} \end{aligned}$$

On simplification and taking logarithm, one may obtain,

$$p[\text{H}] = 12.52 + \log[\text{Al(OH)}_4^-] \quad \dots \text{ (iv)}$$

$p[H]$ of the solutions containing specified concentrations of $Al^{3+}(aq)$ and $[Al(OH)_4^-](aq)$ ions may now be calculated using the relations (iii) and (iv), which respectively, represent the solubility of $Al(OH)_3$ in weakly acidic and weakly alkaline solutions.

$Al^{3+}(aq)$ (mol.lit ⁻¹)	$p[H]$ [Eqn. (iii)]	$[Al(OH)_4^-](aq)$ (mol.lit ⁻¹)	$p[H]$ [Eqn. (iv)]
1.00	3.33	0.01	10.52
0.75	3.37	0.05	11.22
0.50	3.43	0.10	11.52
0.25	3.53	0.25	11.92
0.10	3.66	0.50	12.20
0.05	3.76	0.75	12.40
0.01	4.00	1.00	12.52

Using the above data, one may construct the solubility - $p[H]$ curve (Fig 2.2) of $Al(OH)_3$.

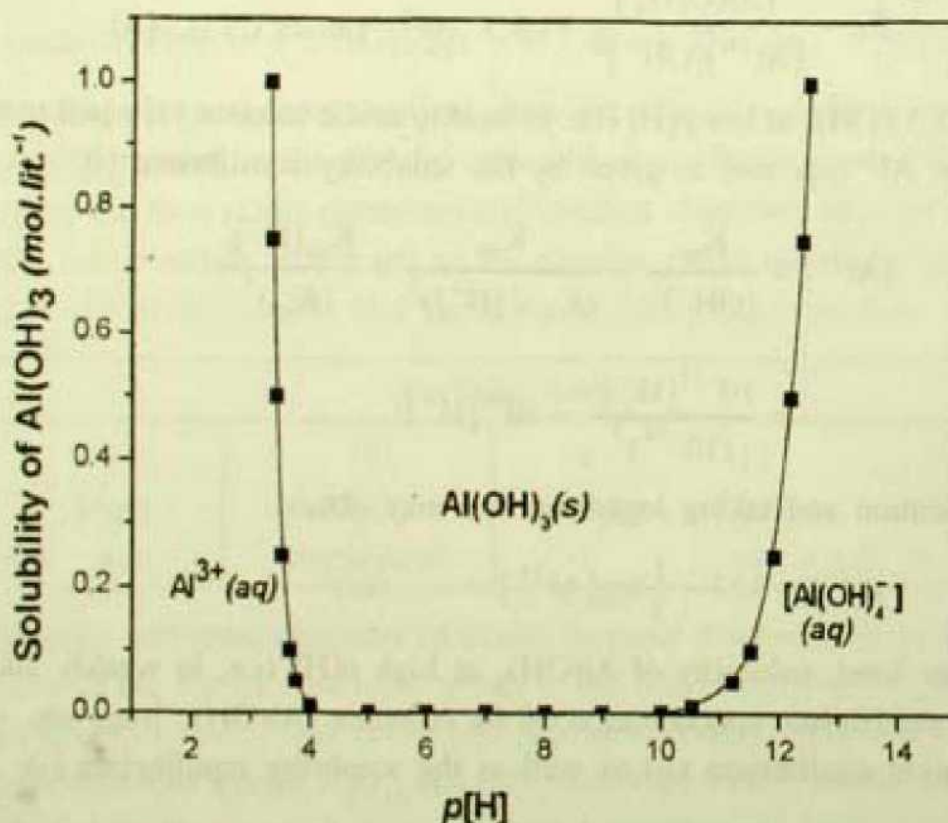


Fig. 2.2. Solubility of $Al(OH)_3$ as a function of $p[H]$

2.4 Oxidation-Reduction Reactions and Redox Equilibria

(a) Definitions

In qualitative inorganic analysis we come across several reactions which may be collectively classified as *oxidation-reduction reactions*. Oxidation-reduction reactions occur concurrently, i.e., when one substance is oxidized, another substance is reduced.

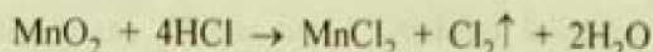
Examples (2.30)

- (1) Reaction of Cl_2 -water with KBr and KI solutions in which bromide (Br^-) and iodide (I^-) ions are oxidized to their elemental forms, which dissolve in organic solvents (CHCl_3 , CCl_4) to produce characteristically coloured organic layers:



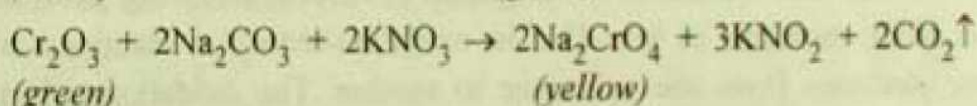
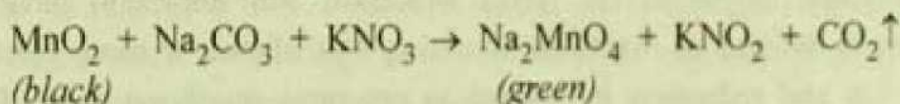
In these reactions Cl_2 is reduced to Cl^- ions.

- (2) Dissolution of black MnO_2 in HCl to produce MnCl_2 with evolution of greenish yellow Cl_2 gas.

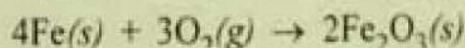


A similar reaction takes place in the preliminary test for chloride when a sample containing a ionic chloride salt is heated with hot concentrated H_2SO_4 in pressence of MnO_2 . Conc. H_2SO_4 displaces HCl from the chloride salt, HCl is then oxidized to Cl_2 by MnO_2 , according to the above reaction. In these reactions HCl is oxidized to Cl_2 and MnO_2 is reduced to MnCl_2 .

- (3) Fusion test for Mn and Cr salts is another well known example of oxidation - reduction reaction. In this test, the samples containing Mn and Cr salts are strongly heated to fusion with a (1:1) mixture of anhydrous Na_2CO_3 and K_2CO_3 (*fusion mixture*) containing some KNO_3 . In the fused melt, KNO_3 oxidizes chromium compounds to yellow coloured chromate (CrO_4^{2-}) ion, manganese compounds to green coloured manganate (MnO_4^{2-}) ion and itself is reduced to nitrite.



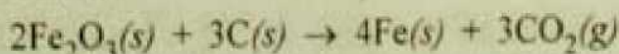
According to historical definition, oxidation refers to addition of oxygen to an element to form an oxide, e.g. (i) rusting of iron,



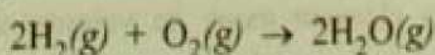
- (ii) burning of coal to produce carbon dioxide and heat energy,



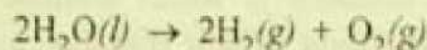
Reduction is referred to the reactions involving removal or loss of oxygen from the oxide of an element to yield the element itself, e.g. carbon reduction of iron ore (hematite, Fe_2O_3) in the extraction of iron,



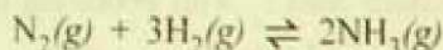
In the burning of H_2 gas in oxygen to produce vapours of H_2O molecules, hydrogen is oxidized and oxygen is reduced,



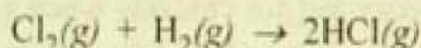
On the other hand, electrolysis of acidified liquid water sets free hydrogen and oxygen in their elemental states,



These reactions give clues to another definition of oxidation-reduction reaction, in terms of hydrogen, instead of oxygen. According to this definition, loss of hydrogen from a compound is oxidation and addition of hydrogen to an element or a compound is reduction. Thus, production of NH_3 from the reaction between N_2 gas and H_2 gas (*Haber's process*) is reduction of nitrogen by hydrogen,



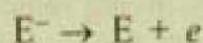
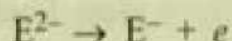
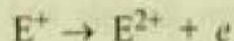
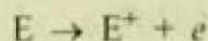
Formation of HCl from the reaction between Cl_2 gas and H_2 gas is reduction of chlorine by hydrogen,



Since oxidation and reduction reactions occur concurrently, in all these reactions, in which elemental hydrogen is transformed into hydrogen containing compounds through its reactions with these non metallic elements, hydrogen is oxidized. To accomodate all these types of reactions, the definitions of oxidation-reduction reactions have been subsequently broadened. According this broad definition, the term oxidation refers to those reactions which involve addition of oxygen or any electronegative (non-metallic) element to an element or a compound, or, loss of hydrogen or any electropositive or a metallic element from a compound. Similarly the term reduction refers to the reactions in which hydrogen or a metallic element is added to an element or a compound, or, oxygen or an electronegative element is lost from a compound.

In modern chemistry language, the terms oxidation and reduction have much wider meanings. Oxidation is defined as reactions involving loss of one or more electrons from an atom, molecule or ion and reduction is defined as reactions involving gain of one or more electrons by an atom, molecule or ion. That is, oxidation-reduction reactions involve transfer of one or more electrons from one substance to another. The oxidation-reduction reactions, hereafter, *redox-reactions*, for an element E may be visualized as follows:

Oxidation of E $\rightarrow$



$\leftarrow$ *Reduction of E*

where, E , E^+ , E^{2+} , E^- and E^{2-} stand for the zero, +1, +2, -1 and -2 oxidation states of the element E . Zero oxidation state of an element means its elemental state. Positive oxidation states of an element mean its valence states after loss of one or more electrons from its elemental state. Similarly negative oxidation states of an element mean its valence states after gain of

one or more electrons to its elemental state. *Oxidation states* of an element are often referred to as *oxidation numbers*, indicating the number of electrons lost or gained by an atom of an element to attain a particular oxidation state. Thus, E , E^+ , E^{2+} , E^- , E^{2-} represent the 0, +1, +2, -1 and -2 oxidation numbers of an atom of the element E . Positive and negative oxidation numbers of an element do not imply cationic or anionic charges. These numbers simply indicate whether an atom of an element is electron rich or electron poor. A positive oxidation number indicates the atom of the element has undergone oxidation through loss of one or more electrons. In a redox reaction it will tend to be reduced by gaining one or more electrons. In a negative oxidation number, the atoms of the element are electron rich due to gain of one or more electrons through a reduction reaction. In a redox reaction it will tend to be oxidized by losing one or more electrons. That is, in a redox reaction, oxidation numbers of the reacting atoms or those of certain atoms in the reacting molecules and ions, undergo change. Since oxidation-reduction reactions are complementary, so if the oxidation number of one atom of an element is increased, oxidation number of an atom of another element must decrease in such a manner that the net increase in oxidation number of the atoms undergoing oxidation reaction is equal to the net decrease of oxidation number of the atoms undergoing reduction. Thus, it is possible to identify a reaction as a redox reaction from the changes of oxidation numbers of certain atoms in the reactant molecules and ions.

It is, therefore, essential to assign oxidation numbers to the atoms constituting the reactant and product molecules/ions in a reaction, for identifying it as a redox reaction.

The following *General rules* are applicable in assigning oxidation numbers to atoms in molecules and ions:

1. Oxidation number of a free or uncombined atom, (i.e., in its elemental state) is zero(0), which may be represented by writing zero(°) at the right superscript after the symbol of the atom or molecule of the element. As for example:

<i>Atoms:</i>	Na°	H°	S°	Cl°	N°	Ba°	Ne°
<i>Molecules:</i>	H_2°	Cl_2°	O_2°	N_2°	P_4°	S_8°	O_3°

2. Oxidation number of a monoatomic ion is equal to its charge : As for example,

<i>Monoatomic ions:</i>	Na^+	Mg^{2+}	Al^{3+}	N^{3-}	O^{2-}	Cl^-
<i>Oxidation number:</i>	+1	+2	+3	-3	-2	-1

3. Metallic elements and hydrogen have usually positive oxidation numbers, and non metallic elements usually have negative oxidation numbers in combination.

In assigning the oxidation number to non-metallic elements the following priority rules are followed:

(i) Oxidation number (O.N.) of hydrogen in combination with non-metallic elements is (+1) and with metallic elements it is (-1). As for example:

<i>Compound:</i>	HCl	NH_3	NaH	CaH_2
<i>O.N. of H:</i>	+1	+1	-1	-1

(ii) Except in peroxo and superoxo compounds, oxidation number of oxygen in combination is always (-2) . Oxidation number of oxygen can be positive in F-O compounds.

<i>Compound:</i>	H ₂ O	HO-OH	HO ₂	NaOH	CaO	CO ₂	OF ₂	O ₂ F ₂
<i>O.N. of oxygen:</i>	-2	-1, -1	-1/2	-2	-2	-2	+2	+1

(iii) Oxidation number of fluorine in all its compounds is (-1) . Oxidation numbers of other halogens (Cl, Br, and I) in combination are usually (-1) , except their compounds with more electronegative oxygen and fluorine i.e., in oxyhalides and in interhalogen compounds with F or with a more electronegative halogen.

<i>Molecule/ion :</i>	HCl	HOCl	Cl ₂ O	NaClO ₄	ClF ₃	ICl ₃	KBrO ₃
<i>O.N. of halogens:</i>	(-1)	$(+1)$	$(+1)$	$(+7)$	$(+3)(-1)$	$(+3)(-1)$	$(+5)$

4. Oxidation number of an atom in a polyatomic ion or a molecule is the same as its oxidation number in a monoatomic ion. As for example, oxidation number of H is $(+1)$ and of O is (-2) in different molecules/ions:

<i>Molecule/ion</i>	H ₂ O	OH ⁻	NH ₃	SO ₄ ²⁻	NO ₂	NO ₂ ⁻	HOCl
<i>O.N. of H:</i>	+1	+1	+1	...	...	...	+1
<i>O.N. of O:</i>	-2	-2	...	-2	-2	-2	-2
<i>O.N. of other elements:</i>	...	...	-3	+6	+4	+3	+1

5. Oxidation number of a metallic element in combination is usually positive, except in some hydrides GeH₄[Ge (-4) , H $(+1) \times 4$], carbonyl/nitrosyl/and dinitrogen complexes:

^{(-1)} K(N ₂) Co	^{(-3)} ^{$(+1) \times 3$} Mn(NO) ₃ (CO)	^{(-1)} [Ni ₂ (CO) ₆] ²⁻
^{(-1)} ^{$(+1)$} Co(CO) ₃ (NO)	^{(-1)} [Mn(CO) ₅] ⁻¹	^{(-2)} [Mo(CO) ₅] ²⁻
	^{(-1)} [Mn(CO) ₄ PR ₃] ⁻	^{(-2)} [W(CO) ₅] ²⁻

6. Oxidation number of a radical or ion is equal to its electrical charge with proper sign.

<i>Radical/ion :</i>	Na ⁺	Cl ⁻	NH ₄ ⁺	SO ₄ ²⁻	O ₂ ²⁻	O ₂ ⁻
<i>Oxidation number:</i>	+1	-1	+1	-2	-2	-1

7. Oxidation number of a molecule or a compound is zero. That is, sum of the oxidation numbers of the constituent atoms, each multiplied by the number of atoms of the element in one molecule/molecular formula of the compound will be zero.

Examples: (2.31)

(1) H₂O

Oxidation number of the constituent atoms : H $(+1)$, O (-2)

∴ Oxidation number of H₂O molecule:

$$= (+1) \times 2 + (-2) \times 1 = +2 - 2 = 0$$

(2) CaCl_2

Oxidation number of the constituent atoms : $\text{Ca}(+2)$, $\text{Cl}(-1)$

$\therefore$ Oxidation number of CaCl_2 :

$$= (+2) \times 1 + (-1) \times 2 = +2 - 2 = 0$$

(3) $\text{KCl.MgCl}_2.2\text{H}_2\text{O}$

Oxidation number of the constituent atoms : $\text{K}(+1)$, $\text{Mg}(+2)$, $\text{Cl}(-1)$, $\text{H}(+1)$, $\text{O}(-2)$

$\therefore$ Oxidation number of $\text{KCl.MgCl}_2.2\text{H}_2\text{O}$:

$$\begin{aligned} &= [(+1) \times 1 + (-1) \times 1] + [(+2) \times 1 + (-1) \times 2] + 2[(+1) \times 2 + (-2) \times 1] \\ &= 0 + 0 + 0 = 0 \end{aligned}$$

(4) Find the oxidation numbers of S in H_2SO_4 , H_2SO_3 and H_2S .

Let the oxidation numbers of sulfur in H_2SO_4 , H_2SO_3 and H_2S be x , y and z . Since the oxidation number of a compound/molecule is zero, therefore,

$$\text{for } \text{H}_2\text{SO}_4 : (+1) \times 2 + x + (-2) \times 4 = 0 \quad \therefore x = +6$$

$$\text{for } \text{H}_2\text{SO}_3 : (+1) \times 2 + y + (-2) \times 3 = 0 \quad \therefore y = +4$$

$$\text{for } \text{H}_2\text{S} : (+1) \times 2 + z = 0 \quad \therefore z = -2$$

(5) Find the oxidation number of S in SO_4^{2-} ion and SO_3^{2-} ion.

Let the oxidation number of S in SO_4^{2-} and SO_3^{2-} ions be x and y respectively. Then,

$$\text{for } \text{SO}_4^{2-} : x + (-2) \times 4 = -2 \quad \therefore x = +6$$

$$\text{for } \text{SO}_3^{2-} : y + (-2) \times 3 = -2 \quad \therefore y = +4$$

(6) Find the oxidation number of N in HNO_3 , HNO_2 , NH_3 and NH_4Cl .

Let the oxidation number of N in HNO_3 , HNO_2 , NH_3 and NH_4Cl be equal to p , q , r and s respectively, then,

$$\text{for } \text{HNO}_3 : (+1) \times 1 + p + (-2) \times 3 = 0 \quad \therefore p = +5$$

$$\text{for } \text{HNO}_2 : (+1) \times 1 + q + (-2) \times 2 = 0 \quad \therefore q = +3$$

$$\text{for } \text{NH}_3 : (+1) \times 3 + r = 0 \quad \therefore r = -3$$

$$\text{for } \text{NH}_4\text{Cl} : (+1) \times 4 + s + (-1) \times 1 = 0 \quad \therefore s = -3$$

(7) Find the oxidation number of oxygen in H_2O , H_2O_2 , HO_2 , O_3 .

Let the oxidation number of O in H_2O , H_2O_2 , HO_2 and O_3 be p , q , r and s respectively, then,

$$\text{for } \text{H}_2\text{O} : (+1) \times 2 + p = 0 \quad \therefore p = -2$$

$$\text{for } \text{H}_2\text{O}_2 : (+1) \times 2 + q \times 2 = 0 \quad \therefore q = -1$$

$$\text{for } \text{HO}_2 : (+1) \times 1 + r \times 2 = 0 \quad \therefore r = -1/2$$

$$\text{for } \text{O}_3 : s \times 3 = 0 \quad \therefore s = 0$$

(8) Find the oxidation number of Mn in MnO_2 , KMnO_4 , Na_2MnO_4 and MnCl_2 .

Let the oxidation number of Mn in MnO_2 , KMnO_4 , Na_2MnO_4 and MnCl_2 be a , b , c and d respectively, then,

$$\text{for } \text{MnO}_2 : a + (-2) \times 2 = 0 \quad \therefore a = +4$$

$$\text{for } \text{KMnO}_4 : (+1) + b + (-2) \times 4 = 0 \quad \therefore b = +7$$

$$\text{for } \text{Na}_2\text{MnO}_4 : (+1) \times 2 + c + (-2) \times 4 = 0 \quad \therefore c = +6$$

$$\text{for } \text{MnCl}_2 : d + (-1) \times 2 = 0 \quad \therefore d = +2$$

(9) Find the oxidation number of Cr in Cr_2O_3 , K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$.

Let the oxidation number of Cr in Cr_2O_3 , K_2CrO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ be x , y and z , respectively, then,

$$\text{for } \text{Cr}_2\text{O}_3 : (x) \times 2 + (-2) \times 3 = 0 \quad \therefore x = +3$$

$$\text{for } \text{K}_2\text{CrO}_4 : (+1) \times 2 + y + (-2) \times 4 = 0 \quad \therefore y = +6$$

$$\text{for } \text{K}_2\text{Cr}_2\text{O}_7 : (+1) \times 2 + z \times 2 + (-2) \times 7 = 0 \quad \therefore z = +6$$

The above mentioned rules often appear insufficient in assigning the oxidation numbers of elements in their compounds having more than one atom of the particular element linked by different types of chemical bonds. These situations are particularly common in case of organic molecules in which the atoms of the same element (e.g. C, N) are linked by different types of chemical bonds and exist in different oxidation numbers. Among the inorganic compounds the following are common :

Examples (2.32)

(1) **Ammonium nitrate NH_4NO_3 .** In assigning oxidation number to N atoms in this type of compounds, advantage is taken of certain of its chemical properties. Since it is a salt, it ionizes to give NH_4^+ and NO_3^- ions, oxidation number(n) of N in these two ions are different:

$$\text{for } \text{NH}_4^+ : (n) + (+1) \times 4 = +1 \quad \therefore n = -3$$

$$\text{for } \text{NO}_3^- : (n) + (-2) \times 3 = -1 \quad \therefore n = +5$$

(2) Some times structural information gives clues to the oxidation number of an element of which more than one atom are present in the stoichiometric formula of a compound.

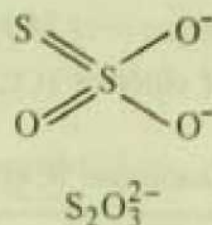
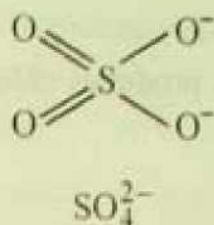
Consider the following compounds of sulfur, each containing two atoms of sulfur :

Sodium thiosulfate : $\text{Na}_2\text{S}_2\text{O}_3$

Potassium pyrosulfate : $\text{K}_2\text{S}_2\text{O}_7$

Potassium peroxodisulfate : $\text{K}_2\text{S}_2\text{O}_8$

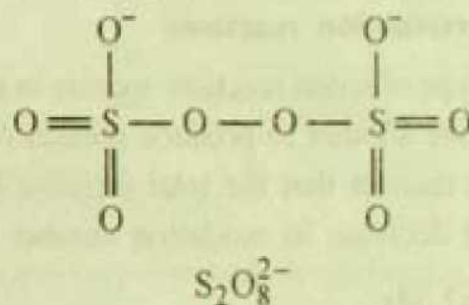
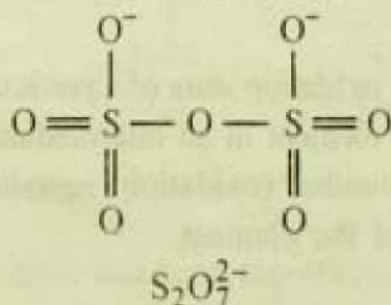
As the names imply, thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ion is like sulfate (SO_4^{2-}) ion in which one O atom is replaced by one S atom.



When an atom in a particular molecule or ion is linked by a chemical bond to another atom of the same element (i.e. *catenation*), oxidation number of each atom of the element for such a chemical bond is taken as zero. So the oxidation number of the terminal S atom in $\text{S}_2\text{O}_3^{2-}$ ion is zero. Oxidation number of the central S atom for linking with the terminal S atom is also zero. Since the central S atom is also bonded with three atoms of O and overall charge of the ion is -2 , therefore, the oxidation number(s) of the central S atom in $\text{S}_2\text{O}_3^{2-}$ ion will be $+4$.

$$[0 + s + (-2) \times 3 = -2 \quad \therefore s = +4]$$

Pyrosulfate ($\text{S}_2\text{O}_7^{2-}$) and peroxodisulfate ($\text{S}_2\text{O}_8^{2-}$) consist of two sulfate groups linked through a common oxo bridge and a peroxo bridge respectively.



Since the oxidation number of O atom in a oxo group (O^{2-}) is (-2) and that in a peroxogroup (O_2^{2-}) is (-1) , oxidation number(s) of S in both these ions is $+6$.

$$\text{S}_2\text{O}_7^{2-} = \text{O}_3\text{S}(\text{O}^-)\text{SO}_3 : (-2) \times 3 + s + (-2) + s + (-2) \times 3 = -2 \quad \therefore s = +6$$

$$\text{S}_2\text{O}_8^{2-} = \text{O}_3\text{S}(\text{O}_2^{2-})\text{SO}_3 : (-2) \times 3 + s + (-2) + s + (-2) \times 3 = -2 \quad \therefore s = +6$$

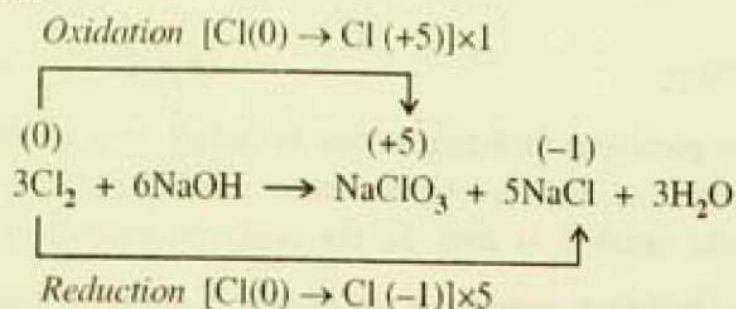
Elements existing in more than one oxidation states, apart from their elemental states of zero oxidation number, may undergo two other types of redox reactions, called *disproportionation reactions* and *comproportionation reactions*.

Disproportionation reactions

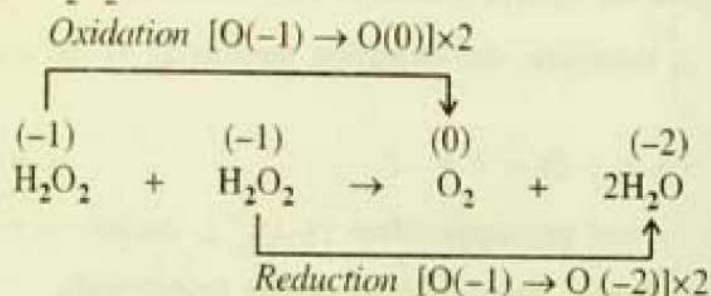
In this type of redox reaction two or more species of the same element in the same oxidation state react to produce more than one species of the element in different oxidation states, that are higher and lower than the oxidation state of the reactant species in such a manner that the total increase in oxidation number (oxidation) is equal to the total decrease in oxidation number (reduction).

Examples (2.33)

- (1) Disproportionation of chlorine (Cl_2^0) in presence of alkali produces chlorate (ClO_3^-) and chloride (Cl^-) ions.



- (2) Disproportionation of H_2O_2 .

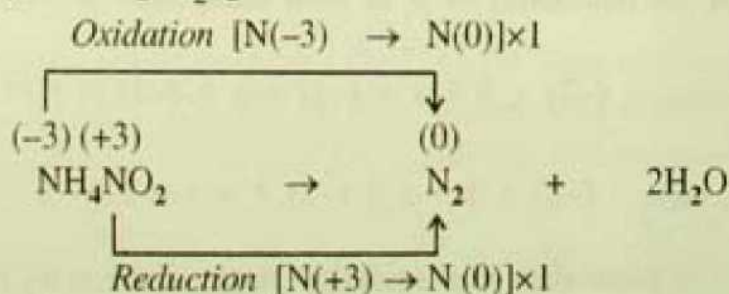


Comproportionation reactions

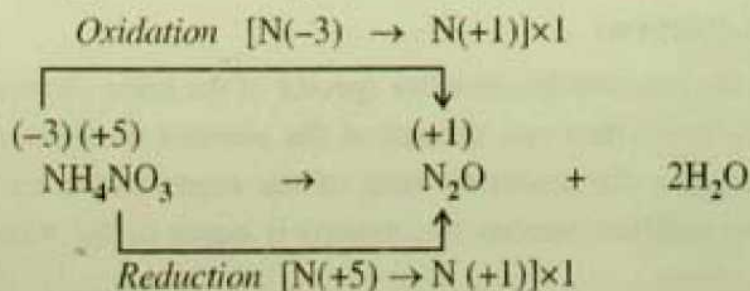
In this type of redox reaction, species in more than one oxidation state of a particular element react with one another to produce species containing the element in an intermediate oxidation state in the manner that the total increase in oxidation number (oxidation) remains the same as the total decrease in oxidation number (reduction) of the element.

Examples (2.34)

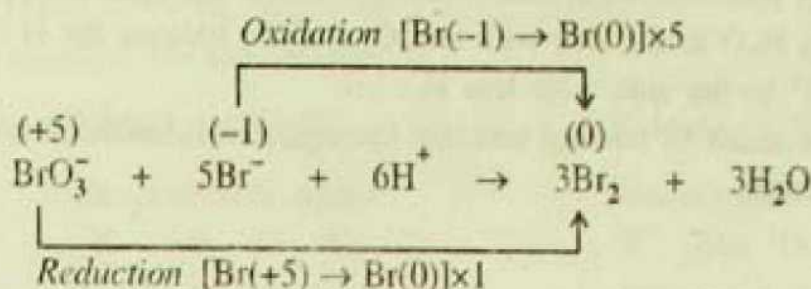
- (1) Ammonium nitrite (NH_4NO_2) is not a stable compound due to comproportionation of NH_4^+ ion and NO_2^- ion, producing N_2 gas:



- (2) Thermal decomposition of solid ammonium nitrate, NH_4NO_3 (**Explosive**) produces nitrous oxide gas, N_2O , as NH_4^+ ion and NO_3^- ion comproportionate.

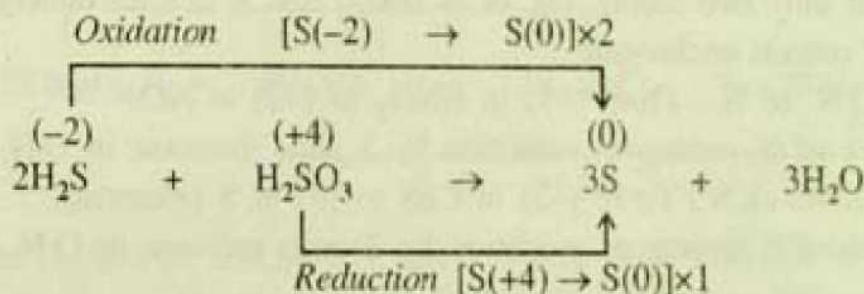


- (3) In acidic solution bromate (BrO_3^-) ion and bromide (Br^-) ion comproportionate to liberate bromine (Br_2).



Similar comproportionation reaction also takes place between iodate (IO_3^-) ion and iodide (I^-) ion with liberation of iodine (I_2) in neutral and weakly acidic medium.

- (4) Colloidal sulfur is formed if H_2S - water is added to a an aqueous solution of a sulfite salt or SO_2 - water (H_2SO_3). Sulfide (S^{2-}) ion and sulfite (SO_3^{2-}) ion comproportionate to produce elemental sulfur (S^0) in colloidal form.



Disproportion and comproportionation reactions are very common in qualitative inorganic analysis.

(b) Balancing Chemical Equations of Redox Reactions by Oxidation Number Method (O.C. Johnson, 1880)

The oxidation number concept may be applied to balance the chemical equations of redox reactions applying the following useful rules:

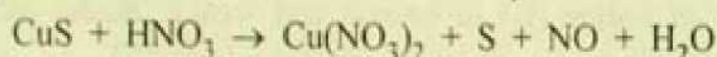
- Write the reactants and the products of the reaction in the format of a chemical equation.
- Assign oxidation numbers (O.N.) to all the atoms on both sides of the equation.
- Inspect which atom(s) on the reactant side is (are) undergoing change in their oxidation numbers in transforming to the products.
- Identify the atoms which undergo increase in oxidation number (oxidation i.e. reductants). Identify the atoms which undergo decrease of oxidation number (reduction, i.e. oxidants).
- Multiply the stoichiometric coefficients of the oxidant and the reductant by appropriate integers to make the total increase of oxidation number of the reductant equal to the total decrease of oxidation number of the oxidant.

- (vi) Inspect the skeleton equation thus deduced and introduce proper coefficients to the formula of the compounds/ions which are neither oxidized nor reduced.
- (vii) For redox reactions in acidic solution, balance the equation for O (oxygen) atoms by adding H_2O to the side with less O, and the balance for H (hydrogen) atoms by adding H^+ to the side with less H.
- (viii) Check the result by making sure that the equation is balanced both for atoms as well as for charge.

Examples (2.35)

(1) Dissolution of CuS in HNO_3 .

Incomplete equation showing the reactants and products:



Atoms on reactant and product sides : Cu S H N O

O.N. of atoms on the reactant side : +2 -2 +1 +5 -2

O.N. of atoms on the product side : +2 0 +1 +5, +2 -2

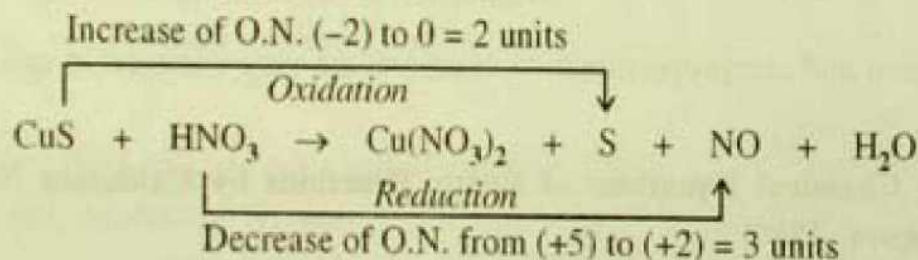
Thus O.N. of only two atoms, viz, N in HNO_3 and S in CuS undergo change. O.N. of the other atoms remain unchanged.

Change of O.N. of N : From (+5) in HNO_3 to (+2) in NO .

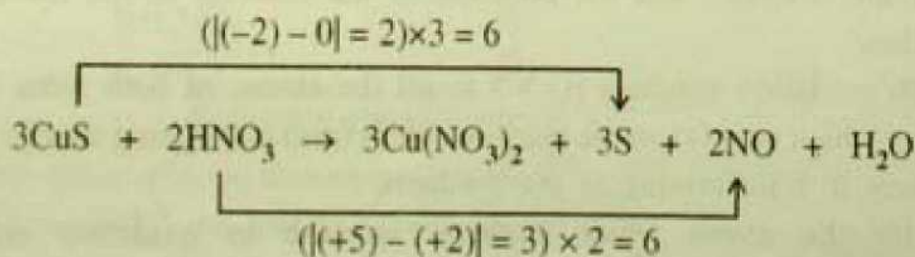
$\therefore$ Each atom of N undergoes reduction by 3 units decrease in O.N.

Change in O. N. of S : From (-2) in CuS to (0) in S (element).

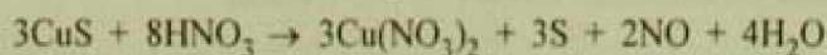
$\therefore$ Each atom of S undergoes oxidation by 2 units increase in O.N.

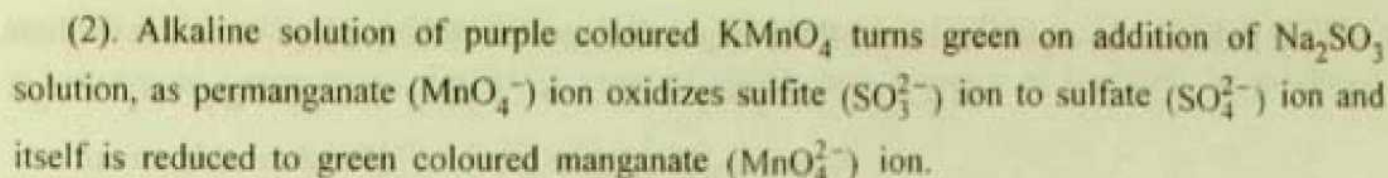


Therefore, the decrease in O.N. of the N-atom will be balanced by the increase in O.N. of the S-atom by multiplying the coefficient of HNO_3 by 2 and that of CuS by 3.



Now, formation of each $Cu(NO_3)_2$ requires $2HNO_3$. So, $3Cu(NO_3)_2$ will require $6HNO_3$. The equation is balanced by adding $6HNO_3$ to the reactant side and consequently 3 more H_2O on the product side, since the only H-containing reactant is HNO_3 and the only H-containing product is H_2O . Therefore, the balanced equation for the reaction is,





The unbalanced equation for the reaction is,



Reactant side atoms

K Mn O Na S

Oxidation Number: (+1) (+7) (-2) (+1) (+4)

Change in O.N.: $\text{Mn}(+7) \rightarrow \text{Mn}(+6)$

$$\text{S}(+4) \rightarrow \text{S}(+6)$$

Product side atoms

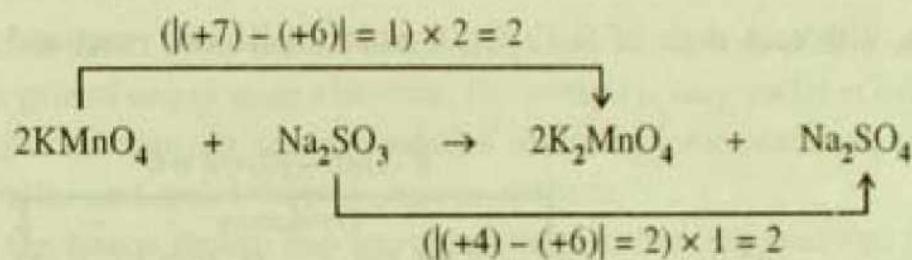
K Mn O Na S

 $(+1) (+6) (-2) (+1) (+6)$

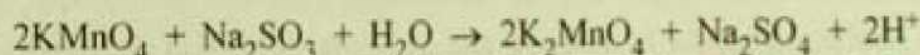
1 unit decrease per Mn atom

2 units increase per S atom.

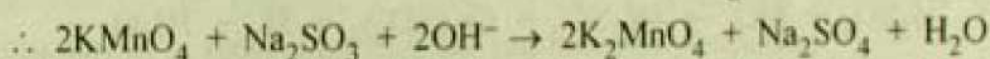
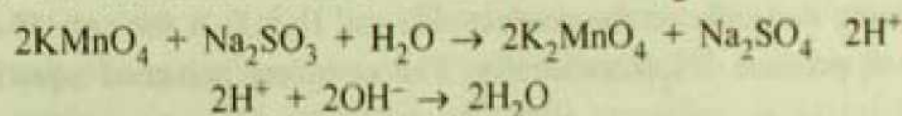
Therefore, decrease in O.N. of Mn atom will be balanced by the increase in O.N. of S atom by multiplying KMnO_4 by 2 and Na_2SO_3 by 1.



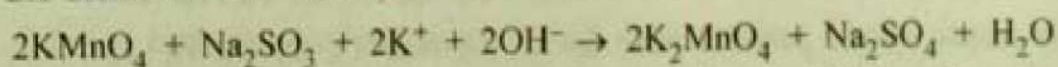
Now, number of O atom on L.H.S. = 11 and on the R. H. S. = 12. To balance the number of O atoms on both sides, add 1 H_2O to the L.H.S. This produces 2H^+ on the R.H.S.



Since the reaction medium is alkaline, 2H^+ ions will react with 2OH^- ions to produce $2\text{H}_2\text{O}$ molecules. So add 2H^+ and 2OH^- ions to the L.H.S. and $2\text{H}_2\text{O}$ to the R.H.S.



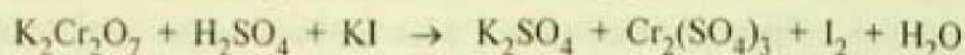
The equation is balanced except in the number of K atoms and charge. Number of K atoms on the L.H.S. is 2, whereas on the R.H.S., it is 4. So, 2 atoms of K should be added to the L.H.S. Charge on the L.H.S. is (-2) for 2OH^- ions, whereas, charge on the R.H.S. is zero. The equation can be balanced in respect of number of atoms and charge, by adding 2K^+ ions instead of 2K atoms on the L.H.S.,



The K^+ and OH^- ions come from KOH as the solution is alkaline. Therefore, the final complete balanced form of the equation is,



(3) Balance the equation of the following redox reaction taking place in acidic medium.



Reactant side atoms						Product side atoms					
K	Cr	O	H	S	I	K	Cr	O	H	S	I
Oxidation number(O.N.): (+1) (+6) (-2) (+1) (+6) (-1)						(+1) (+3) (-2) (+1) (+6) (0)					
Change in O.N.: Cr (+6) → Cr (+3)						3 units decrease per Cr atom.					
I (-1) → I (0)						1 unit increase per I atom.					

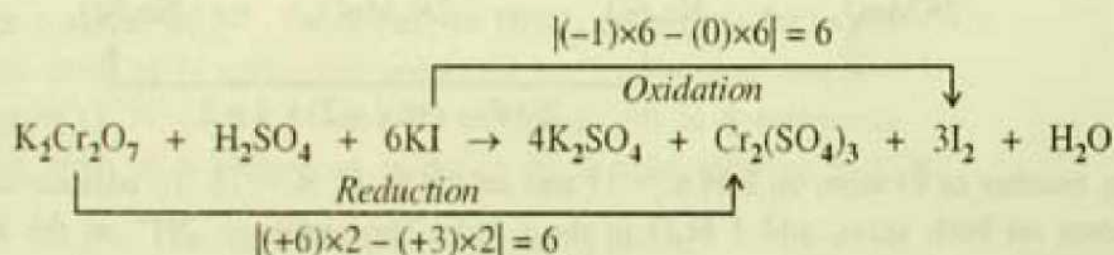
∴ Decrease in O. N. per Cr atom = (Increase in O.N. per I atom) × 3.

Since, dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ion involves 2 Cr atoms,

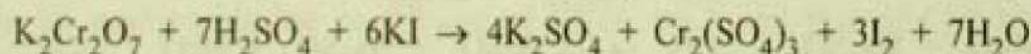
∴ Decrease in O. N. of 2 Cr atoms in $\text{Cr}_2\text{O}_7^{2-}$ ion = (Increase in O.N. per I atom) × 3 × 2

$$\therefore [\text{Cr}_2\text{O}_7^{2-}] = [\text{I}^-] \times 6$$

Therefore, with each mole of $\text{K}_2\text{Cr}_2\text{O}_7$, 6 moles of KI will react and 3 moles of I_2 will be produced.

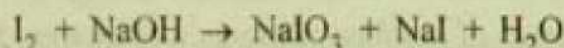


For 8 K^+ and 2 Cr^{3+} ions on the R.H.S. to exist as sulfate salts, as many as 7 sulfate (SO_4^{2-}) ions are required, which require $7\text{H}_2\text{SO}_4$ to be added to the L.H.S. Since H_2O is the only H-containing molecule on the product side and H_2SO_4 is the only H-containing reactant, so $7\text{H}_2\text{SO}_4$ will produce $7\text{H}_2\text{O}$ molecules. The complete balanced equation is, therefore,



(4) Iodine undergoes disproportionation to iodate and iodide in presence of hot conc. NaOH. Balance the equation for the reaction by oxidation number method.

The unbalanced equation for the reaction is,



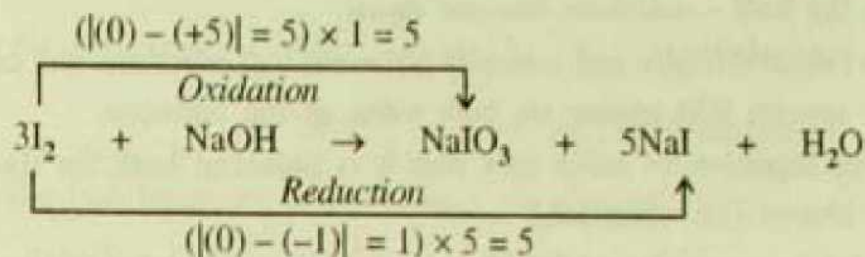
O.N. of atoms on the reactant side: I(0), Na(+1), O(-2), H(+1)

O.N. of atoms on the product side: I(+5, -1), Na(+1), O(-2), H(+1)

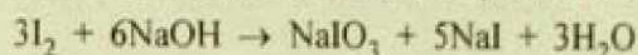
∴ Change in O.N. is undergone by I atoms only.

For oxidation of I(0) in I_2 to I(+5) in IO_3^- ion, increase in O.N. per I atom is by 5 units. For reduction of I(0) in I_2 to I(-1) in I^- ion, decrease in O.N. per I atom is by 1 unit.

Therefore, IO_3^- and I^- will be produced in the ratio 1:5. That is, if 6 moles of $\text{I}(0)$ or 3 moles of I_2 react with NaOH , 1 mole of NaIO_3 and 5 moles of NaI will be produced.



Since the number of atoms of Na on the R.H.S. is 6, so there should be 6NaOH on the L.H.S. and consequently $3\text{H}_2\text{O}$ on the R.H.S., which automatically balances the number of O-atoms on both sides of the equation. The complete balanced equation is, therefore,



(c) Ion-Electron Method of Balancing Chemical Equations of Redox Reactions (Jette and La Mer, 1927)

This method is based upon the definitions of oxidation as loss of one or more electrons and reduction as gain of one or more electrons. The method is very useful in balancing chemical equations of redox reactions in aqueous solution involving ionic reactants, as we often come across in qualitative and quantitative inorganic analyses.

The overall reaction is broken into two components, called half-reactions for oxidation and half-reaction for reduction. Each half-reaction is first separately balanced. The two separately balanced half-reactions are then added to obtain the equation for the overall reaction after multiplying with appropriate integer coefficients, so that the number of electrons lost by the reductants (i.e., oxidation) is exactly equal to the number of electrons gained by the oxidants (i.e., reduction). When the reactions take place in aqueous solution, in addition to the ions derived from the oxidants and reductants and the electrons, molecules of H_2O , H^+ and OH^- ions are also present in the system and may be utilized in balancing the half-reactions (i.e. *partial equations*). The unit of change in oxidation or reduction reaction is a change by one electron, denoted by the symbol, ' e^- '. The following schematic procedure is useful for balancing the equation of a redox reaction by ion-electron method:

- (i) Write the unbalanced net ionic equation of the reaction, putting the reactants on the left hand side and the products on the right hand side.
- (ii) Find which atoms of the reactants are oxidized and which atoms are reduced.
- (iii) Split the net reaction into two half-reactions (partial equations), one representing oxidation and the other representing reduction.
- (iv) Balance both the half-reactions for all atoms except H and O atoms.
- (v) Balance each half-reaction for O-atom, by adding required number of H_2O molecules to the side with less O-atoms and balance for H-atom by adding H^+ ion to the side with less H-atoms.
- (vi) Balance each half-reaction for charge. For this purpose, add required number of

electrons, e , (i.e. negative charge) to the side with greater positive charge. Multiply both half-reactions with appropriate integer factors, so that the electron (e) counts of both the half - reactions become equal.

- (vii) Add the two atomically and ionically balanced half-reactions and cancel the electrons and the species that appear on both sides of the equation.
- (viii) Check the equation to make sure that it is balanced both for the atoms (i.e. ions) and for charge (i.e. electrons).

Let us consider as examples, a few reactions we come across in qualitative inorganic analysis.

Examples (2.36)

(1) Test for iodide

When Cl_2 -water is added to a colourless solution of KI, iodine is liberated, which turns the solution brown coloured.

The unbalanced equation of the reaction is,



Change of oxidation number : $\text{Cl}(0)$ to $\text{Cl}(-1)$, $\text{I}(-1)$ to $\text{I}(0)$

So iodide (I^-) ion is oxidized to iodine (I_2) and chlorine (Cl_2) is reduced to chloride (Cl^-) ion.

$\therefore$ Half-reaction for oxidation : $\text{I}^- \rightarrow \text{I}_2$ (unbalanced)

Half-reaction for reduction : $\text{Cl}_2 \rightarrow \text{Cl}^-$ (unbalanced)

Now, on balancing both the half-reactions for atoms and also for charge we obtain,

for oxidation : $2\text{I}^- \rightarrow \text{I}_2 + 2e$ (balanced)

for reduction : $\text{Cl}_2 + 2e \rightarrow 2\text{Cl}^-$ (balanced)

Adding the two balanced half-reactions, we obtain,



The equation is completed by adding appropriate number of positive ions (here, 2K^+ ions) on both sides. Therefore, the final form of the balanced equation is,



(2) Test for Hg

When a solution of mercuric salt (say HgCl_2) is treated with stannous chloride (SnCl_2) solution, white precipitate of mercurous chloride (Hg_2Cl_2) appears, which gradually transforms to grey-black metallic mercury (Hg) in presence of excess of SnCl_2 .

The unbalanced equation for the reaction is,



$\therefore$ Oxidation: $\text{Sn}(+2) \rightarrow \text{Sn}(+4)$

Reduction: $\text{Hg}(+2) \rightarrow \text{Hg}_2(+2)$



Half-reaction for oxidation : $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$ (unbalanced)

$\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e$ (balanced)

Half-reaction for reduction : $\text{Hg}_2^{2+} \rightarrow \text{Hg}_2^{2+}$ (unbalanced)

$2\text{Hg}^{2+} + 2e \rightarrow \text{Hg}_2^{2+}$ (balanced)

Now, adding the two balanced half-reactions we obtain,

$2\text{Hg}^{2+} + \text{Sn}^{2+} \rightarrow \text{Hg}_2^{2+} + \text{Sn}^{4+}$ (balanced)

The complete equation is obtained on adding appropriate number of Cl^- ions on both sides of the equation:

$2\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$

For reduction of Hg_2Cl_2 to metallic Hg, the half-reactions are,

Reduction: $\text{Hg}_2^{2+} + 2e \rightarrow 2\text{Hg}$

Oxidation: $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+} + 2e$

$\therefore$ Net reaction $\text{Hg}_2^{2+} + \text{Sn}^{2+} \rightarrow 2\text{Hg} + \text{Sn}^{4+}$

The complete balanced equation for the reaction is,

$\text{Hg}_2\text{Cl}_2 + \text{SnCl}_2 \rightarrow 2\text{Hg} + \text{SnCl}_4$

(3) Dissolution of PbS in hot dilute HNO_3 in Group-IIA analysis

The unbalanced equation for the reaction is,

$\text{PbS} + \text{HNO}_3 \rightarrow \text{Pb}(\text{NO}_3)_2 + \text{NO} + \text{S} + \text{H}_2\text{O}$

Oxidation: $\text{S}^{2-} \rightarrow \text{S}^0$ (unbalanced)

$\text{S}^{2-} \rightarrow \text{S}^0 + 2e$ (balanced)

Reduction: $\text{NO}_3^- \rightarrow \text{NO}$ (unbalanced)

$\text{NO}_3^- + 4\text{H}^+ \rightarrow \text{NO} + 2\text{H}_2\text{O}$ (atomically balanced, ionically unbalanced)

$\text{NO}_3^- + 4\text{H}^+ + 3e \rightarrow \text{NO} + 2\text{H}_2\text{O}$ (atomically and ionically balanced)

Multiplying the oxidation half-reaction by 3 and reduction half-reaction by 2, the number of electrons lost becomes equal to number of electrons gained:

$3\text{S}^{2-} \rightarrow 3\text{S}^0 + 6e$

$2\text{NO}_3^- + 8\text{H}^+ + 6e \rightarrow 2\text{NO} + 4\text{H}_2\text{O}$

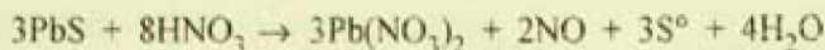
Net reaction: $2\text{NO}_3^- + 8\text{H}^+ + 3\text{S}^{2-} \rightarrow 2\text{NO} + 3\text{S}^0 + 4\text{H}_2\text{O}$

$\therefore 2\text{NO}_3^- + 8\text{H}^+ + 3\text{PbS} \rightarrow 3\text{Pb}^{2+} + 2\text{NO} + 3\text{S}^0 + 4\text{H}_2\text{O}$

3S^{2-} come from 3PbS , which also supply 3Pb^{2+} ions. 3Pb^{2+} ions require 6NO_3^- ions for charge neutralization. 8H^+ come from 8HNO_3 of which 2HNO_3 are reduced to 2NO . The



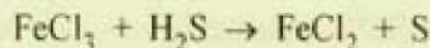
remaining 6HNO_3 supply 6NO_3^- which neutralize the charge of 3Pb^{2+} . Therefore, the completed and balanced equation is,



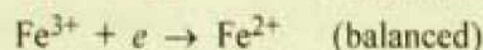
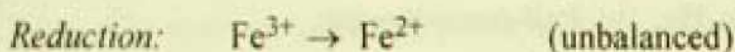
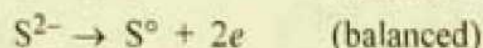
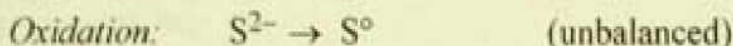
Dissolution of CuS , CdS in nitric acid also takes place according to this stoichiometry.

(4) H_2S reduces FeCl_3 with precipitation of colloidal sulfur

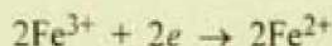
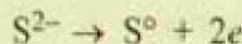
Unbalanced equation of the reaction is,



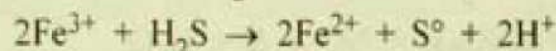
The half-reactions are:



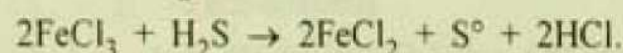
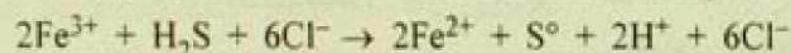
Multiplying the oxidation half-reaction by 1 and reduction half-reaction by 2, and then adding the two half-reactions, the number of electrons lost becomes equal to the number of electrons gained.



Since S^{2-} ion comes from H_2S , the next step is,

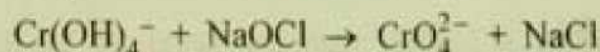


Since the positive charge on both sides of the equation is 6, the equation is completed by adding 6Cl^- ion in appropriate form on both sides of the equation:

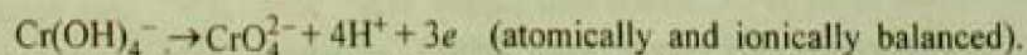
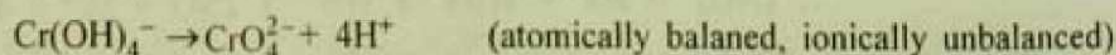
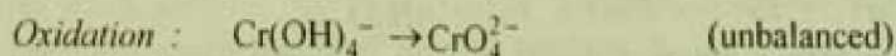


(5) Oxidation of Chromite, $\text{Cr}(\text{OH})_4^-$ ion to chromate, CrO_4^{2-} ion by alkaline sodium hypochlorite (NaOCl) in aqueous solution (cf. Group -IIIA analysis, Sect. 7.8).

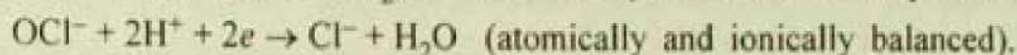
The unbalanced equation for the reaction is,



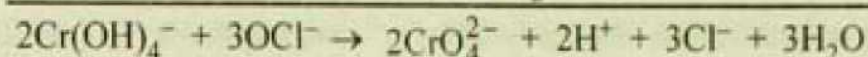
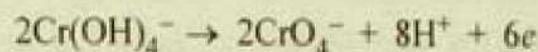
The half-reactions are,



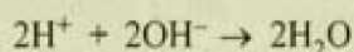
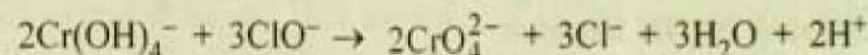
Reduction:



Number of electrons lost in oxidation reaction becomes equal to number of electrons gained in reduction reaction, on multiplying the oxidation half-reaction with 2 and reduction half-reaction with 3.



The equation is now atomically and ionically balanced. But still it does not represent the actual picture of the reaction. Since the reaction takes place in alkaline medium, H^+ ions can not be set free in this reaction. So the 2H^+ ions on the R.H.S. of the equation should react with 2OH^- ions present in the alkaline reaction medium to produce $2\text{H}_2\text{O}$ molecules.



This equation is not only atomically and ionically balanced, it also reflects a true picture of the reaction. Charge on both sides is -7 . The charge is neutralized by adding 7Na^+ ions to both the sides. Thus, the final form of the equation is,

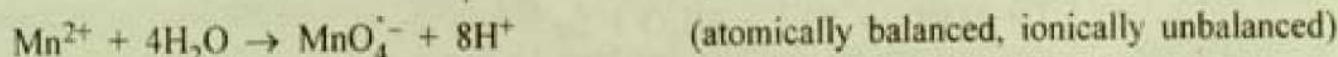


(6) Oxidation of Mn(II) salt to permanganate (MnO_4^-) by sodium bismuthate (NaBiO_3) in nitric acid medium

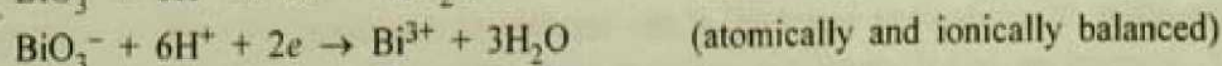
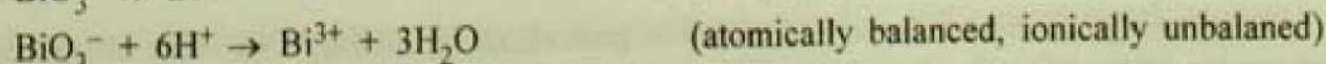
The unbalanced equation for the reaction is,



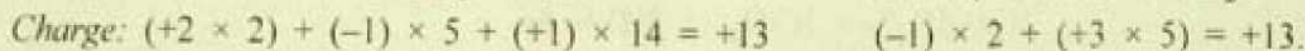
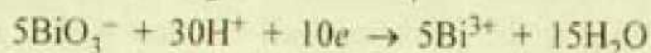
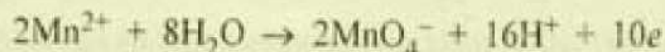
Half-reaction for oxidation :



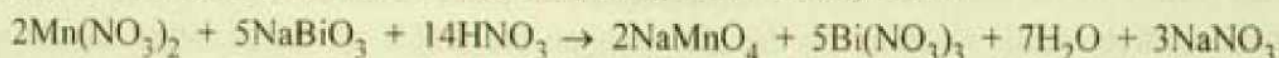
Half-reaction for reduction:



Number of electrons lost in oxidation becomes equal to the number of electrons gained in reduction on multiplying the oxidation half-reaction with 2 and reduction half-reaction with 5. Adding the two balanced half-equations and cancelling the like terms, we obtain the net equation for the reaction:



14H^+ ions come from 14HNO_3 , 2Mn^{2+} ions requires 4NO_3^- ions and 5BiO_3^- ions require 5Na^+ for charge neutralization. Similarly 2MnO_4^- ions require 2Na^+ or 2H^+ ions and 5Bi^{3+} ions require 15NO_3^- ions for charge neutralization. Adding appropriate number of cations and anions to both sides, we obtain the completely balanced equation:

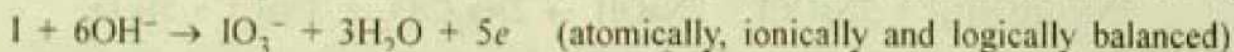
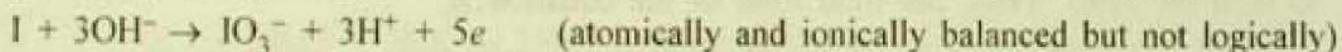
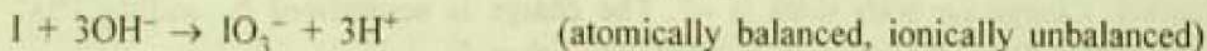


(7) Disproportionation of iodine (I_2) to produce iodate (IO_3^-) and iodide (I^-) on reaction with hot concentrated NaOH solution

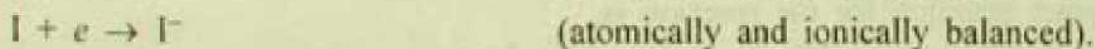
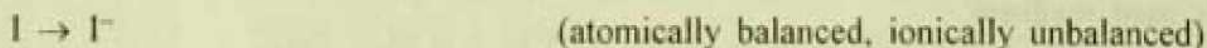
The unbalanced equation for the reaction is,



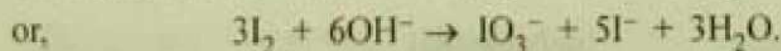
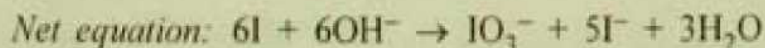
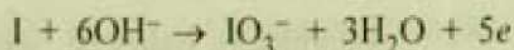
Oxidation half-reaction :



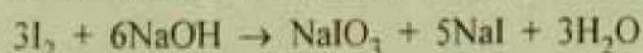
Reduction half-reaction:



Number of electrons lost in oxidation becomes equal to the number of electrons gained in reduction on multiplying the oxidation half-reaction with 1 and reduction half-reaction with 5. On adding these two balanced half-equations we obtain the net equation:



Now, charge on both sides is -6 , which is neutralized by adding 6Na^+ ions to both sides of the equation. The complete equation of the reaction is therefore,



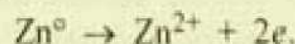
(d) Energetics of Oxidation - Reduction Reactions

(i) Galvanic Cell Potential and Free Energy Change

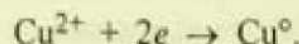
Oxidation involves loss of electrons, reduction involves gain of electrons and electric current is essentially a flow of electrons. Thus, as oxidation - reduction reactions are associated with electron transfers, flow of electric current from one electrode to the other in a cell is also associated with oxidation-reduction reactions. Let us consider a galvanic cell of which one of the two electrodes consists of a Zn rod immersed into an aqueous solution of ZnSO_4 , and another electrode consists of a Cu rod immersed into an aqueous solution of CuSO_4 . If the two electrolytes (ZnSO_4 and CuSO_4) solutions are connected by a Na_2SO_4 -agar salt-bridge and the two electrodes (Zn and Cu) are connected by a metallic wire, a stream of electrons (*current*) flows through the external circuit from the Zn-electrode to the Cu-electrode. According to Nernst (1888), when a metal is brought into contact with a solution one of its salts, two electrochemical phenomena set in. One is the tendency of metal atoms to pass into the solution as metallic ions, leaving one or more electrons on the metal rod, thereby making the metal electrode negatively charged with respect to the solution. This tendency is called *electrolytic solution pressure* of the metal. The second phenomenon is the tendency of the metallic ions in the salt solution to be deposited as metal atoms on the metal electrode, thereby making the metal electrode positively charged, relative to the solution. This tendency is called *osmotic pressure of the solution*. Electrolytic solution pressure is a characteristic property of the metallic element itself, it does not depend upon the amount of metal or shape of the metallic electrode, whereas, osmotic pressure of the solution depends upon the concentration of the metallic ions in the solution. The metallic ions released into the solution due to electrolytic solution pressure, can not move far away from the metal electrode because of their comparatively large cationic charge. In fact, because of the electrostatic attraction of the negatively charged metal electrode, the positively charged metallic ions are held to form a *electrical double layer* around the metal electrode, as the anions (here, the SO_4^{2-} ions) arrange themselves around the layer of the positively charged metal ions. Similarly, because of osmotic pressure, as the metal electrode becomes positively charged with respect to the solution, it attracts the negatively charged SO_4^{2-} ions to form an electrical double layer around it, as the positively charged metallic ions tend to arrange themselves around the layer of SO_4^{2-} ions. As the electrolytic solution pressure (p_e) of the metal is opposed by the osmotic pressure (p_o) of the solution, an electrochemical equilibrium is reached, when only a minute amount of the metal has passed into solution as metallic ions or a minute quantity of the metallic ion has deposited as metal atom on the electrode. The potential difference established between the metal and the solution of its salt at equilibrium is called the *electrode potential*, more appropriately, *single electrode potential* of the metal-metal ion system. Magnitude of the electrode potential depends upon the concentration of the metal ion in the salt solution and also upon the nature of the metallic element itself and temperature. The sign

of the electrode potential is conventionally adopted as the sign of the charge of the metal electrode, and that is governed by the relative magnitudes of p_e and p_o :

(i) if $p_e > p_o$ The metal becomes negatively charged relative to the solution as oxidation of metal atom to metal ion predominates. This occurs with the Zn/ZnSO_4 electrode,

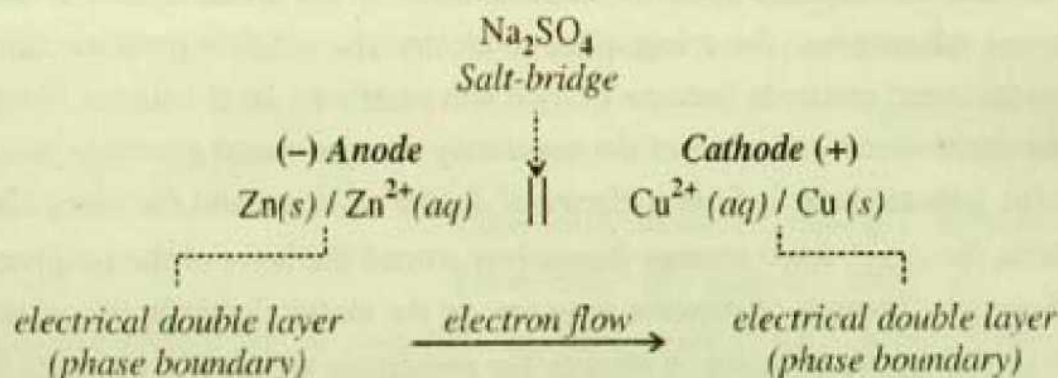


(ii) if $p_e < p_o$ The metal becomes positively charged relative to the solution as reduction of metal ions to metal atoms predominates. This occurs with the Cu/CuSO_4 electrode,



(iii) if $p_e = p_o$ The metal remains uncharged in the solution. This occurs with noble metals, e.g. Pt, Au etc.

Thus, when the metal is positively charged with respect to the solution, the electrode potential has a positive sign and when the metal is negatively charged with respect to the solution, the electrode potential is negative. Therefore, for the galvanic cell under consideration (*Daniel cell*) the Cu/CuSO_4 electrode is the positive electrode, where reduction of Cu^{2+} ion to Cu atom takes place (i.e., *cathode*). The Zn/ZnSO_4 electrode is the negative electrode, where oxidation of Zn atom to Zn^{2+} ion takes place (i.e., *anode*). The flow of current in this cell is thus, due to flow of electrons from the electron rich Zn electrode (anode) to the electron deficient Cu electrode (cathode) through the external circuit:



Such a flow of electrons through the external circuit from Zn electrode to Cu electrode takes place because the electrons have lower energy when on Cu than on Zn atom (atomic radii : Cu (1.28 Å), Zn (1.38 Å)). The driving force that pushes the negative electrons away from the negative electrode (*anode*) and pulls them toward the positive electrode (*cathode*) is an electrical potential, called *electromotive force (emf)* of the cell. The *emf* (E) of a galvanic cell is defined as a positive quantity, which in SI unit, is expressed as *volt* (V), and is related to the SI unit of energy (*joule*, J) and electric charge (*coulomb*, C) according to the relation:

$$1\text{J} = 1\text{C} \times 1\text{V} = 1\text{V.C}$$

where, C is the amount of charge (in *coulomb*) transferred when a current of 1 *ampere*



flows for 1 second (S). When 1C of charge is transferred between two electrodes differing in electrode potential by 1V, 1J of energy is released for useful work. Since 1 watt (W) is equal to 1 J. S⁻¹, this energy is also equal to 1 watt.

The cell potential, i.e., *emf* (E) is an electrical quantity. It is directly proportional to the *free energy change* (ΔG), which is a thermodynamic quantity of the cell reaction. These two quantities are related by the equation:

$$\Delta G = -nFE$$

where, n = number of moles of electrons transferred in the reaction, F = *faraday* (*Faraday constant*), the electric charge carried by one mole of electrons (96,485 C/mole of electron, rounded off to 96500 C/mole of electron). As the unit of E is volt (V) and that of F is *coulomb* (C), therefore, the unit of ΔG is *volt.coulomb* (V.C.) i.e. *joule* (J). Since the cell *emf* (E) is a positive quantity, and for a spontaneous cell reaction ΔG has to be negative, a minus sign is put in the relation between these two quantities to indicate their opposite signs.

When the reactants and the products in a cell reaction are present in their *standard states* i.e. solutes at 1 *molar* concentrations (more accurately *activities*), gases at a partial pressure of 1 *atm.*, solids and liquids in their pure forms, all at a specified temperature, usually 25°C, the *emf* or cell potential under this condition is defined as *standard cell potential* (E°), which is related to the *standard free energy change* (ΔG°) by the equation,

$$\Delta G^\circ = -nFE^\circ$$

Example (2.37)

(i) Find the standard free energy change for the cell reaction:

$\text{Zn}(s) + \text{Cu}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$ at 25°C if the standard cell potential is 1.10V.

$$\begin{aligned}\Delta G^\circ &= -nFE^\circ = -2(\text{mol. of } e) \times \frac{96500\text{C}}{(\text{mol. of } e)} \times (1.10\text{V}) \times \left(\frac{1\text{J}}{1\text{C.V}}\right) \\ &= 212,300 \text{ J} = 212.3 \text{ kJ} = 50.5 \text{ k.Cal} \quad (\because 1 \text{ Cal.} = 4.2 \text{ J})\end{aligned}$$

(ii) Nernst equation for single electrode potential

Nernst (1889) expressed the potential difference existing between a metal and a solution of its ion, i.e., a single *electrode potential* (E) by the relation,

$$E = \frac{RT}{nF} \ln \frac{p_o}{p_e}$$

where, R is the *Universal gas constant* expressed in electrical units, F is faraday and n is the valency of the ion, T is absolute temperature. Substituting $R = 1.989 \times 4.2\text{J} = 8.3538 \text{ V.C.K}^{-1}$, $T = 298\text{K}$ (25°C), $F = 96500 \text{ coulomb.mol}^{-1}$ and expressing natural logarithm to logarithm to base 10 by multiplying with the factor 2.303, the above expression for 25°C becomes,

$$E = \left(\frac{8.3538 \text{ V} \cdot \text{C} \cdot \text{K}^{-1} \times 298 \text{ K} \times 2.303}{n(\text{mol}) \cdot 96500 \text{ C} \cdot \text{mol}^{-1}} \right) \log_{10} \frac{p_o}{p_e}$$

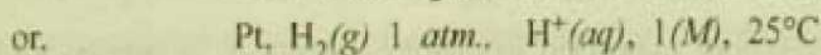
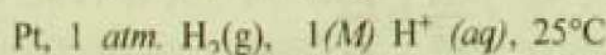
$$E = \frac{0.0594}{n} \log_{10} \frac{p_o}{p_e} (\text{V})$$

Since osmotic pressure (p_o) is directly proportional to the concentration (c) of the solution and absolute temperature (T) by the relation, $p_o = cRT$, the electrode potential, E , at a particular temperature will, therefore, depend upon the concentration (more correctly activity) of the metal ions. For a univalent ion ($n = 1$), if the concentration is increased by 10 times, the electrode potential E will increase by 0.0594 volt (~ 0.06 volt). For a divalent ion ($n = 2$), under the above condition, the electrode potential will increase by $0.0594/2 = 0.0297$ volt (~ 0.03 volt). The higher is the concentration of the metal ions in the solution, the higher will be the osmotic pressure and the electrode potential will have higher (more positive, less negative) value, and greater will be the tendency of the metal ions in solution to be reduced to metal atoms by taking up electrons from the metal electrode. On the other hand, the electrolytic solution pressure (p_e) of the metal atoms is a measure of their tendency to be converted into metal ions, by losing their electrons to the metal electrode (i.e., by oxidation), so, it is a measure of the tendency of the metal atoms to undergo oxidation.

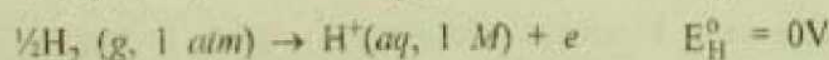
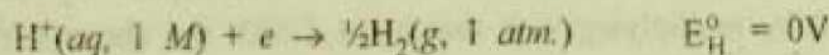
(iii) Standard electrode potential (E°)

There is, however, no known method for experimental determination of single electrode potentials. For the determination of the potential difference between a metal (electrode) and a solution, the electrode under consideration has to be coupled with a *standard reference electrode* of arbitrarily fixed potential to form a *voltic cell*, the *emf* of which can be measured by a voltmeter. Since the *emf* of the cell is the algebraic difference between the two electrode potentials, the electrode potential of the experimental electrode can be calculated. The Universally accepted standard reference electrode used for comparing the potentials of single electrodes, is the *molar or normal hydrogen electrode* (NHE) also called *standard hydrogen electrode* (SHE). The standard hydrogen electrode (SHE) consists of a platinized platinum foil, immersed in a solution of hydrochloric acid, *molar* with respect to hydrogen ions (i.e., hydrogen ions H^+ of unit activity, $a_{\text{H}^+} = 1 \text{ M}$), through which pure hydrogen gas (H_2) is passed at a pressure of 1 atmosphere (1 atm.) and kept at 25°C , the potential of which has been arbitrarily and Universally fixed at zero (0) volt.

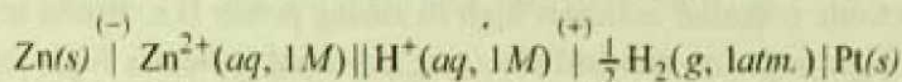
The SHE may be described according to,



The corresponding half-reactions, written in either direction, is assigned an arbitrary potential of zero (0) volt :



Now, if the Zn/ZnSO_4 electrode in which concentration (activity) of $\text{Zn}^{2+}(\text{aq})$ ions is 1 mol.lit^{-1} (i.e. 1 M) is coupled with a SHE, the following *galvanic cell* is formed:



Electromotive force (emf) of the cell (E_{cell}) is the algebraic difference between the standard electrode potentials of the cathode (+) and the anode (−) electrodes.

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E_{\text{cell}}^{\circ} = E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\circ} - E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

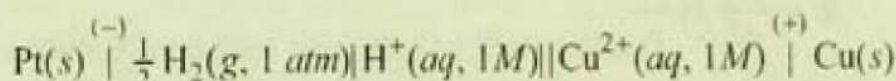
Since, $E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\circ}$ is equal to zero (0), therefore,

$$E_{\text{cell}}^{\circ} = -E_{\text{Zn}^{2+}/\text{Zn}}^{\circ}$$

The measured standard cell potential (E_{cell}°) at 25°C is 0.76 volt .

Therefore, $E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} = -0.76 \text{ volt}$ at 25°C .

Similarly, if the $\text{Cu(s)}/\text{CuSO}_4 (1\text{M})$ electrode is coupled with a SHE, the following *galvanic cell* is formed,



for which the standard *emf* (E_{cell}°) is given by

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\circ}$$

Since, $E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\circ}$ is equal to zero (0), therefore,

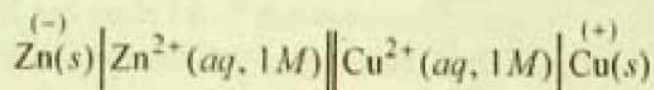
$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ}$$

The measured standard *emf* of this cell at 25°C is 0.34 volt . Therefore, $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} = 0.34 \text{ volt}$ at 25°C .

The *standard electrode potential* of an element may, therefore, be defined as the *emf* of the cell produced when a half-cell (i.e. electrode) consisting of the pure element immersed in a molar solution of its ions (i.e. solution in which the ions are at their unit activity), is coupled with a SHE at 25°C , the standard electrode potential of which is zero (0) *volt*. Standard electrode potentials of some common half-cells at 25°C are listed in Appendix-A8 in which the sign of the potential is the sign of the charge on the electrode. Arranging the standard electrode potentials in decreasing or increasing order, we obtain the *electrode potential series* or *electrochemical series* of the elements. A greater positive value of the potential of a non-metallic element electrode reflects the tendency of the non-metal atom to be transformed into anions and that of a metallic element electrode reflects the tendency of metal cations to be transformed into metal atoms by accepting electrons (reduction). A greater negative value of

the potential (always encountered with metal electrodes) reflects the tendency of the metal atoms to be transformed to metal cations by losing electrons (oxidation). Thus, high positive value of standard electrode potential indicates high oxidizing power (i.e. strong tendency to undergo reduction) and high negative standard electrode potential indicates high reducing power (i.e. strong tendency undergo oxidation).

Now, $E^\circ_{\text{Cu}^{2+}/\text{Cu}}$ and $E^\circ_{\text{Zn}^{2+}/\text{Zn}}$ being known, it is possible to calculate the standard *emf* of the *Daniel cell*,



by neglecting *liquid junction potentials*, and using the relation,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{Cu}^{2+}/\text{Cu}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}} \\ &= +0.34 \text{ V} - (-0.76\text{V}) = 1.10\text{V}. \end{aligned}$$

Based on the two properties, electrolytic solution pressure (p_e) and osmotic pressure (p_o), *Nernst equation* for single electrode potential for electrodes of the types:

$\text{M}^{n+}(aq) + ne \rightleftharpoons \text{M}(s)$ may be splitted into two components:

$$\begin{aligned} E &= \frac{RT}{nF} \ln \frac{p_o}{p_e} \\ &= \frac{RT}{nF} \ln \frac{1}{p_e} + \frac{RT}{nF} \ln p_o \end{aligned}$$

The first term on the R.H.S. involves electrolytic solution pressure (p_e) which is a characteristic property of the electrode material (the metal atoms) and at a particular temperature it is constant for the given element. The second term involves the osmotic pressure (p_o) of the solution, which depends upon the concentration (c), (more accurately activity ' a ') of the ions in the solution ($p_o = aRT \approx cRT$ for dilute solution). The modified form of the above equation may be written as,

$$\begin{aligned} E &= \text{constant} + \frac{RT}{nF} \ln cRT \\ &= (\text{constant} + \frac{RT}{nF} \ln RT) + \frac{RT}{nF} \ln c \\ &= \text{constant} + \frac{RT}{nF} \ln c \end{aligned}$$

When the concentration (more appropriately activity) of the ions in solution is 1 mol.lit^{-1} (i.e. 1 M), the second term on the R.H.S. vanishes. The electrode potential, E , under this condition is a constant for the half-cell (electrode) at a particular temperature. This constant potential is called the *standard electrode potential* of the electrode, and is denoted by the symbol, E° . Thus,

$$E = E^\circ$$

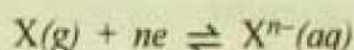
when $c = 1 (M)$. Therefore, the Nernst equation for a metal/metal ion half-cell $M(s)/M^{n+}(aq)$, at a concentration $c \text{ mol.lit}^{-1}$ of the $M^{n+}(aq)$ ions may be written as,

$$E = E^{\circ} + \frac{RT}{nF} \ln c$$

Substituting the values of R , F and T (298 K) and transforming the natural logarithm to logarithm to base 10 by multiplying with 2.303, one obtains the expression for the electrode potential at 25°C ,

$$E = E^{\circ} + \frac{0.059}{n} \log_{10} c$$

Similarly the electrode potential of a non-metal electrode,



will be given by,

$$E = E^{\circ} - \frac{0.059}{n} \log_{10} c$$

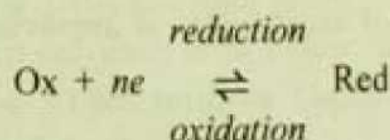
where, c = concentration of $X^{n-}(aq)$ ions in the solution.

Therefore, knowing the E° of a half-cell, it is possible to calculate its electrode potential for any concentration.

(e) Oxidation-Reduction Electrodes and Redox Potentials

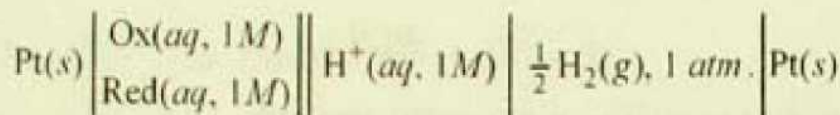
(i) Definition

Oxidation involves loss of electrons and reduction involves gain of electrons. In a system consisting of an oxidant (Ox) and its conjugate reductant or reduction product (Red), a *redox equilibrium* is established between the oxidant, reductant and the electrons:



If an inert electrode such as a platinized platinum foil or a wire is brought into contact with such a redox system, the electrode assumes a definite potential depending upon the position of the equilibrium. If the oxidation tendency is greater than the reduction tendency, that is, if the oxidizing power of the oxidant component is stronger than the reducing power of the conjugate reductant, then the redox system takes up electrons from platinum electrode and the oxidant (Ox) component is transformed to the reductant (Red) component, as a result, the platinum electrode becomes positively charged. If the reducing power of the system is stronger than its oxidizing power, the platinum electrode becomes negatively charged. Such a system consisting of a conjugate oxidant-reductant couple, thus forms a half-cell, called a *redox couple* and in conjunction with an inert metal such as platinum, it constitutes a *redox electrode*. The magnitude of the potential of a redox electrode serves as a measure of the oxidising or reducing power of the redox system. The standard electrode potential of a redox electrode can be obtained in the same manner as the standard potentials of the metal-metal ion electrodes, that

is, by measuring under standard experimental conditions, the potential difference between the platinum electrode and the solution containing the redox couple, relative to a standard reference electrode, such as SHE, potential of which is taken as zero. Under the standard experimental condition, the concentrations (more appropriately activities) of the oxidant and the reductant in the redox half-cell are 1 mol.lit^{-1} , (i.e, 1 M), that is, the ratio of concentrations of oxidant to that of the reductant is unity. The oxidation - reduction cell thus formed, may be described as,



The standard *emf* of the cell is given by,

$$E_{\text{cell}}^{\circ} = E_{\text{ox/red}}^{\circ} - E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\circ} = E_{\text{ox/red}}^{\circ} \quad \left(\because E_{\text{H}^+/\frac{1}{2}\text{H}_2}^{\circ} = 0 \right)$$

The potential measured in this way is the *standard oxidation-reduction potential* or *standard redox potential* of the redox half-cell (electrode). The sign of the standard redox potential, $E_{\text{ox/red}}^{\circ}$, is the sign of the charge on the platinum electrode. Standard redox potentials of some common redox couples are given in Appendix A-8. Redox couples with positive E° values occur at the upper end and those with negative E° values occur at the lower end of the table of standard potentials. Oxidant components of the redox couples of high positive value of standard redox potentials are powerful oxidizing agents and the reductant components of the redox couples with high negative standard redox potentials are powerful reducing agents. Oxidant component of a redox couple occurring upper in the table may oxidize the reductant component of a redox couple occurring lower in the table of standard potentials, provided the difference between the E° values of the couples is appreciable.

Examples (2.38)

(1) Permanganate ion (MnO_4^-) oxidizes Cl^- , Br^- , I^- , Fe^{2+} , $[\text{Fe}(\text{CN})_6]^{4-}$, AsO_3^{3-} in acid medium and itself is reduced to Mn^{2+} ion, since the difference in the E° values ($\Delta E^{\circ} = E^{\circ}(\text{MnO}_4^-/\text{Mn}^{2+}) - E^{\circ}(\text{ox/red})$) are appreciably large.

Redox Couples	$E^{\circ}(\text{ox/red})$ (volt, 25°C)	$\Delta E^{\circ}(\text{volt})$
MnO_4^- , $\text{H}^+/\text{Mn}^{2+}$	+1.51	—
$\frac{1}{2}\text{Cl}_2/\text{Cl}^-$	+1.36	0.15
$\frac{1}{2}\text{Br}_2/\text{Br}^-$	+1.07	0.44
$\text{Fe}^{3+}/\text{Fe}^{2+}$	+0.77	0.74
$\text{AsO}_4^{3-}\text{H}^+ / \text{AsO}_3^{3-}$	+0.56	0.95
$\frac{1}{2}\text{I}_2/\text{I}^-$	+0.53	0.98
$[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$	+0.36	1.15

(2) Bromate (BrO_3^-) ion can oxidize bromide (Br^-) ion to liberate bromine (Br_2) and iodide (I^-) to iodine (I_2), but it can not oxidize chloride (Cl^-) ion to liberate Cl_2 , as the difference in the E° values of BrO_3^- , $\text{H}^+/\frac{1}{2}\text{Br}_2$ and $\frac{1}{2}\text{Cl}_2/\text{Cl}^-$ couples is not appreciably large. It may be noted that all these oxidation reactions by bromate ion take place in dilute acid (HCl) medium.

Redox Couples	$E^\circ(\text{ox/red}), (\text{volt } 25^\circ\text{C})$	$\Delta E^\circ(\text{volt})$
$\text{BrO}_3^-, \text{H}^+/\frac{1}{2}\text{Br}_2$	+ 1.45	...
$\frac{1}{2}\text{Cl}_2/\text{Cl}^-$	+ 1.36	0.09
$\frac{1}{2}\text{Br}_2/\text{Br}^-$	+ 1.07	0.38
$\frac{1}{2}\text{I}_2/\text{I}^-$	+ 0.53	0.92

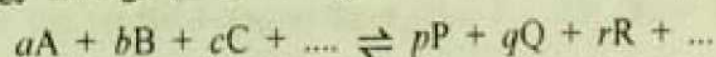
Although the table of standard redox potentials gives information about the feasibility of a redox reaction, but it says nothing about the reaction condition, speed of the reaction, nor does it give any information about the necessity of a catalyst.

As the definition of standard redox potential (E°) implies, it is a property of a redox couple, when both the components, i.e., oxidant and reductant, are present at their unit activities. To apply the E° values for quantitative study of redox reactions, it is convenient to consider that a solution of an oxidant is always associated with some amount of the conjugate reductant whatever small. Similarly, a solution of a reductant is always associated with some amount of the conjugate oxidant whatever small. That is, a solution of Fe^{3+} is always associated with some Fe^{2+} ion, whatever small, so that a $\text{Fe}^{3+}/\text{Fe}^{2+}$ redox couple exists. Similarly, a solution of iodine (I_2) is always associated with some amount of iodide (I^-) ion whatever small, so that the $\frac{1}{2}\text{I}_2/\text{I}^-$ redox couple exists. This concept applies to all redox couples.

(ii) Nernst equation for redox-potentials

The quantitative relationship between redox potential and activities of the reduced and oxidized forms is given by *Nernst equation*, named after the German chemist, Walther H. Nernst (1864-1941), who received the Nobel prize in chemistry in 1920 in recognition of his contribution in chemical thermodynamics.

The free energy change (ΔG) of a generalized chemical reaction,



is expressed by the relation,

$$\Delta G = \Delta G^\circ + RT \ln Q$$

where, ΔG° is the standard free energy change, R is the Universal gas constant, T is absolute temperature and Q is the *reaction quotient*, defined according to,

$$Q = \frac{a_{\text{P}}^p \times a_{\text{Q}}^q \times a_{\text{R}}^r \times \dots}{a_{\text{A}}^a \times a_{\text{B}}^b \times a_{\text{C}}^c \times \dots}$$

where, a_{A} , a_{B} , a_{C} ... and a_{P} , a_{Q} , a_{R} ... etc. are the activities of respective species of the

reactants and the products respectively and the power terms thereof correspond to their stoichiometric coefficients in the balanced chemical equation. Activities of the pure solid and pure liquid components among the reactants and products are constant and their values are considered to be unity. In dilute solution, water is also treated as a pure liquid. Activities of the gaseous reactants and products are taken as their partial pressures and activities of ionic solutes are taken as their molar concentrations, i.e.

$$a_i = []_i f_i$$

where, a_i and $[]_i$ are the activity and molar concentration respectively of the i th species and f_i is its *activity coefficient*. In dilute solution, activity coefficient (f_i) approaches unity and concentration $[]_i$ approaches activity a_i , i.e. $[]_i \approx a_i$.

Free energy change (ΔG) of an electrochemical reaction is given by,

$$\Delta G = -nFE$$

where, n = number of moles of electrons transferred in the reaction, F = *faraday* (Faraday constant), the charge carried by one mole of electrons (96,485 C per mole of electrons, rounded off to 96500 C per mole of electrons) and E is the electrode potential. Under standard condition, i.e. all ionic solutes at 1 *molar* concentrations (more correctly activities), gases at a partial pressure of 1 *atm*, solids and liquids in their pure forms, all at a specified temperature, usually 298K (25°C), the standard free energy change (ΔG°) is related to the standard electrode potential (E°) according to,

$$\Delta G^\circ = -nFE^\circ$$

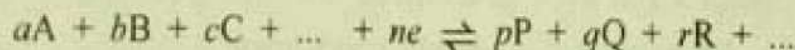
Substituting these relationships in the expression for reaction free energy, one obtains,

$$-nFE = -nFE^\circ + RT \ln Q$$

Dividing both sides by $-nF$, gives the Nernst equation,

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

of a generalized electrode reaction,



Substitution the values of the constants, $R = 8.314 \text{ J. mol}^{-1} \text{ K}^{-1}$, $F = 96485 \text{ C}$, ($\approx 96500 \text{ C}$) at 25°C (298.15 K), and transforming natural logarithm to logarithm to base 10 by multiplying with 2.303 and then rounding off the numerical value of RT/F upto three decimal places, we obtain the simpler form of the Nernst equation for an electrode reaction at this temperature (25°C):

$$E = E^\circ - \frac{0.059}{n} \log_{10} Q$$

where, the electrode potential E is the actual potential difference (*emf*) across a cell consisting of this electrode and a standard hydrogen electrode (SHE).

When the reaction quotient Q is expressed as concentration quotient in place of activities, the thermodynamic standard potential E° is replaced by the *stoichiometric standard potential* E° .

Alternatively, two Nernst equations corresponding to two half-cell reactions can be combined into the Nernst equation for a cell reaction.

$$\Delta E_{\text{cell}} = (E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}) - \frac{0.059}{n} \log_{10} Q.$$

$$\therefore \Delta E_{\text{cell}} = \Delta E^\circ_{\text{cell}} - \frac{0.059}{n} \log_{10} Q.$$

When an electrochemical system is at equilibrium, $\Delta G = 0$, $\Delta E_{\text{cell}} = 0$, and the reaction quotient, Q is equal to the thermodynamic equilibrium constant (K°), which is related to the standard free energy change (ΔG°) according to,

$$\Delta G^\circ = -RT \ln K^\circ$$

Since, $\Delta G^\circ = -nFE^\circ$, therefore,

$$-nFE^\circ = -RT \ln K^\circ$$

$$\therefore E^\circ = \frac{RT}{nF} \ln K^\circ = \frac{2.303RT}{nF} \log_{10} K^\circ$$

Taking $2.303 RT/F$ equal to 0.059 V at 25°C , one obtains,

$$E^\circ = \frac{0.059}{n} \log_{10} K^\circ \text{ in volts at } 25^\circ\text{C}.$$

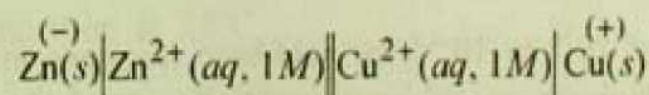
$$\therefore \log_{10} K^\circ = \frac{nE^\circ}{0.059}$$

$$\therefore K^\circ = 10^{nE^\circ/0.059}$$

This relation is very useful for calculating the equilibrium constants of redox reactions in very dilute solutions where accurate measurement of concentration are not feasible.

Example: (2.39)

(1) Calculate the equilibrium constant (K°) for the cell reaction of Daniel cell:

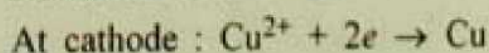
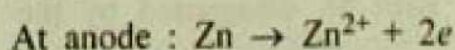


[Given : $E^\circ(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$, $E^\circ(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$]

Here Zn^{2+}/Zn electrode is the anode and Cu^{2+}/Cu electrode is the cathode.

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = +0.34 - (-0.76) = 1.10 \text{ V}.$$

Electrode reactions:



$\therefore$ Number of electrons transferred = $n = 2$

$$\therefore E_{\text{cell}}^{\circ} = \frac{0.059}{n} \log_{10} K^{\circ}$$

$$\therefore \log_{10} K^{\circ} = \frac{n \cdot E_{\text{cell}}^{\circ}}{0.059} = \frac{(2) \times (1.10\text{V})}{(0.059\text{V})} = 37.29$$

$$\therefore K^{\circ} = \text{Inverse log } 37.29 = 10^{37.29} = 1.94 \times 10^{37} \approx 2 \times 10^{37} \text{ at } 25^{\circ}\text{C}.$$

Since the value of the equilibrium constant is very large, the reaction goes essentially to completion. At equilibrium (assuming a dilute solution):

$$K^{\circ} = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 2 \times 10^{37}$$

$$\therefore [\text{Cu}^{2+}] = \frac{[\text{Zn}^{2+}]}{2 \times 10^{37}} = 5 \times 10^{-38} [\text{Zn}^{2+}]$$

that is, when $[\text{Zn}^{2+}]$ is 1(M), $[\text{Cu}^{2+}]$ will be as small as 5×10^{-38} (M). Therefore,

E_{cell}°	positive	$\log_{10} K$	positive	$K > 1$
E_{cell}°	negative	$\log_{10} K$	negative	$K < 1$

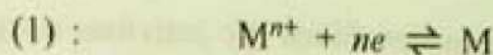
E° values of known redox couples (half-cells) range from +3V for strongest oxidant couple ($\text{F}_2(\text{g}) + 2e \rightarrow 2\text{F}^-(\text{aq})$, $E^{\circ} = 2.87\text{ V}$) to -3V for strongest reductant couple ($\text{Li}^+(\text{aq}) + e \rightarrow \text{Li}(\text{s})$, $E^{\circ} = -3.04\text{V}$) (Appendix A8). E° values outside this range are uncommon. Thus, the span of standard potentialy from +3V to -3V gives a range of E_{cell}° of +6V for the reaction of the strongest oxidizing agent with the strongest reducing agent (i.e. -6V for a reaction between weakest oxidizing agent and the weakest reducing agent). For the transfer of two electrons ($n = 2$) in such reactions, the K values range from very high ($\sim 10^{200}$) to very low ($\sim 10^{-200}$) values :

$$10^{(2)(+6)/0.059} > K = 10^{2E/0.059} > 10^{(2)(-6)/0.059} \\ \approx 10^{200} > K > 10^{-200}$$

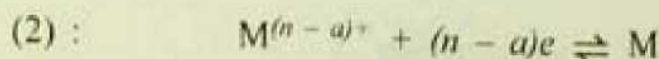
as compared to the range of 10^{14} to 10^{-14} for acid-base reactions in aqueous solution. Therefore, the redox reactions typically go either essentially to completion (K very large) or almost does not take place at all (K very small).

(iii) Redox potentials of adjacent and non-adjacent redox couples

Redox potentials of an element existing in different oxidation states are related to one another. Suppose a metal M exists in two oxidation states M^{n+} and $M^{(n-a)+}$ and each of the two ions form reversible single electrodes with M , designated by the half reactions (1) and (2):

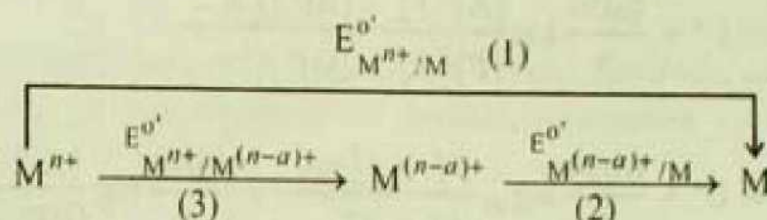


$$E_1 = E^{\circ'}_{M^{n+}/M} + \frac{0.059}{n} \log_{10}[M^{n+}]$$



$$E_2 = E^{\circ'}_{M^{(n-a)+}/M} + \frac{0.059}{n-a} \log_{10}[M^{(n-a)+}]$$

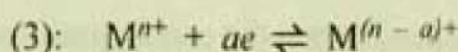
Standard potential of the $M^{n+}/M^{(n-a)+}$ couple (3) is related to the corresponding values of the two terminal couples (1) and (2).



Multiplying E_1 with n and E_2 with $(n-a)$, then subtracting $(n-a)E_2$ from nE_1 and dividing both sides of the equation by ' a ' one obtains the expression,

$$\left[\frac{nE_1 - (n-a)E_2}{a} \right] = \left[\frac{nE^{\circ'}_1 - (n-a)E^{\circ'}_2}{a} \right] + \frac{0.059}{a} \log_{10} \frac{[M^{n+}]}{[M^{(n-a)+}]}$$

which appears to be the Nernst equation for the intermediate redox couple (3):



$$E_3 = E^{\circ'}_{M^{n+}/M^{(n-a)+}} + \frac{0.059}{a} \log \frac{[M^{n+}]}{[M^{(n-a)+}]}$$

Therefore, the stoichiometric standard potential of the redox couple $M^{n+}/M^{(n-a)+}$ may be calculated from the corresponding values of the other two connected couples using the relation:

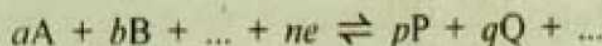
$$E^{\circ'}_{M^{n+}/M^{(n-a)+}} = \frac{nE^{\circ'}_{M^{n+}/M} - (n-a)E^{\circ'}_{M^{(n-a)+}/M}}{a}$$

(f) Formal Potentials

The Nernst equation at 25°C,

$$E = E^{\circ} - \frac{0.059}{n} \log_{10} Q$$

for the generalized half-cell reaction



may be written as,

$$E = E^{\circ} + \frac{0.059}{n} \log_{10} \frac{(a_A)^a (a_B)^b}{(a_P)^p (a_Q)^q}$$

where, the terms have their usual meanings described earlier. Since the activities (a 's) of the reactants and the products are difficult to measure, it is convenient for all practical purposes to replace the activities of the respective species with their equilibrium concentrations $[]$, using the relation

$$\text{activity} = \text{activity coefficient} \times \text{concentration}$$

i.e., $a_i = f_i \times []_i$

and to express the Nernst equation in terms of these quantities :

$$E = E^\circ + \frac{0.059}{n} \log \frac{[A]^a f_A^a \times [B]^b f_B^b \times \dots}{[P]^p f_P^p \times [Q]^q f_Q^q \times \dots}$$

or,
$$E = E^\circ + \frac{0.059}{n} \log_{10} \frac{f_A^a \times f_B^b \times \dots}{f_P^p \times f_Q^q \times \dots} + \frac{0.059}{n} \log \frac{[A]^a \times [B]^b \times \dots}{[P]^p \times [Q]^q \times \dots}$$

Now the ratio of the activity coefficients in the second term on the R.H.S. of the above equation may be replaced by the *mean ionic activity coefficient* $f(\pm)$ of the solution. According to *Debye-Hückel Limiting law* the mean ionic activity coefficient of an electrolytic solution is related to its *ionic strength* (μ) according to the relation,

$$\log f(\pm) = -Az_+z_- \sqrt{\mu} + C\mu$$

where A and C are constants. Ionic strength (μ) depends upon the concentrations and charges of all the ions present in the solution. μ is given by the relation,

$$\mu = \frac{1}{2} \sum c_i z_i^2$$

where, c_i is the analytical concentration, and z_i is the charge of the i th ion present in the solution. In presence of a large excess of an indifferent electrolyte (such as NaClO_4 , Na_2SO_4 , NaNO_3 , KNO_3 etc.), which do not participate in the electrode reaction, the ionic strength (μ) remain practically constant, so that one may assume without any serious error,

$$E^\circ + \frac{0.059}{n} \log \frac{f_A^a \times f_B^b \times \dots}{f_P^p \times f_Q^q \times \dots} = E^{\circ'} \approx \text{Constant} (\because E^\circ \text{ is a constant})$$

and the Nernst equation maybe written in terms of equilibrium concentrations of the reactants and products of the electrode reaction, in the following form,

$$E = E^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[A]^a \cdot [B]^b \times \dots}{[P]^p \cdot [Q]^q \times \dots}$$

where, $E^{\circ'}$ is the *stoichiometric standard electrode potential*, whereas, E° is a *thermodynamic quantity*.

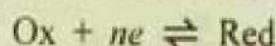
A more useful form of the Nernst equation may be written by replacing the equilibrium

concentrations []'s by the analytical concentrations c 's of the components of the electrode reaction, when the stoichiometric standard electrode potential (E°) is called the *formal potential* (E^f) of the electrode reaction:

$$E = E^f + \frac{0.059}{n} \log_{10} \frac{c_A^a \times c_B^b \times \dots}{c_P^p \times c_Q^q \times \dots}$$

Thus, the formal potential E^f is the potential of the half-cell reaction for which the analytical concentrations of the reactants and products as appearing in the Nernst equation are all unity (i.e. 1 M)

The Nernst equation for the half-cell reaction of a redox electrode, consisting of an oxidized form (Ox) and a reduced form (Red) of an element, represented by the half-reaction,



where protons (H^+) are not involved and H_2O molecules are not produced, may be written in the following different forms:

$$\begin{aligned} E &= E^\circ - \frac{RT}{nF} \ln Q \\ &= E^\circ - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}} \\ &= E^\circ - \frac{0.059}{n} \log_{10} \frac{a_{\text{Red}}}{a_{\text{Ox}}} \quad (\text{at } 25^\circ \text{ C}) \\ &= E^\circ + \frac{0.059}{n} \log_{10} \frac{a_{\text{Ox}}}{a_{\text{Red}}} \\ &= E^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]}{[\text{Red}]} \\ &= E^f + \frac{0.059}{n} \log \frac{c_{\text{Ox}}}{c_{\text{Red}}} \end{aligned}$$

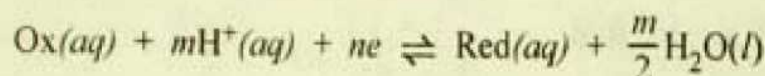
where, E° and $E^{\circ'}$ are *thermodynamic and stoichiometric standard electrode potentials* and E^f is the *formal potential* of the redox couple, n is the number of electrons transferred, a_{Ox} , $[\text{Ox}]$, c_{Ox} are the activity, equilibrium concentration and analytical concentration of the Ox form and a_{Red} , $[\text{Red}]$ and c_{Red} are the corresponding quantities of the Red form, Q is the reaction quotient, $a_{\text{Red}}/a_{\text{Ox}}$.

For this type of system, the value of the electrode potential (E) is solely determined by the ratio $c_{\text{Ox}}/c_{\text{Red}}$. For a system with $n = 1$, the value of E at 25°C for different values of $c_{\text{Ox}}/c_{\text{Red}}$ are shown below:

$$n = 1$$

$c_{\text{Ox}}/c_{\text{Red}}$	E (volt)
100	$E^f + 0.118$
10	$E^f + 0.059$
1	E^f
$\frac{1}{10}$	$E^f - 0.059$
$\frac{1}{100}$	$E^f - 0.118$

Expressions for electrode potentials (E) at 25°C for redox systems of the type,



involving H^+ ions and H_2O molecules, (omitting the charges if any of the Ox and Red forms for simplicity) may be written in the following forms:

$$\begin{aligned} E &= E^\circ + \frac{0.059}{n} \log_{10} \frac{a_{\text{Ox}} a_{\text{H}^+}^m}{a_{\text{Red}}} \\ &= E^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}][\text{H}^+]^m}{[\text{Red}]} \\ &= E^{\circ'} + \frac{0.059}{n} \log_{10} [\text{H}^+]^m + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]}{[\text{Red}]} \\ &= \left\{ E^{\circ'} - \frac{0.059m}{n} p[\text{H}] \right\} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}]}{[\text{Red}]} \\ &= E^f + \frac{0.059}{n} \log_{10} \frac{c_{\text{Ox}}}{c_{\text{Red}}} \end{aligned}$$

The formal potential E^f at a specified hydrogen ion concentration may be calculated using the relation,

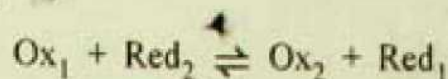
$$E^f = E^{\circ'} + \frac{0.059m}{n} \log_{10} [\text{H}^+] = E^{\circ'} - \frac{0.059m}{n} p[\text{H}]$$

For dilute solutions, $E^{\circ'}$ may be taken as E° and $[\text{H}^+]$ as c_{H^+} without any serious error. Therefore, for dilute solutions,

$$E^f \approx E^\circ + \frac{0.059m}{n} \log_{10} c_{\text{H}^+} \approx E^\circ - \frac{0.059m}{n} p[\text{H}]$$

(g) Equilibrium Constants of Oxidation - Reduction Reactions

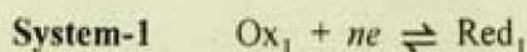
The stoichiometric equilibrium constant i.e., the concentration quotient (K) of an oxidation-reduction reaction,



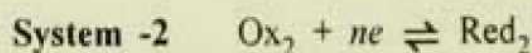
is defined by,

$$K = \frac{[\text{Ox}_2][\text{Red}_1]}{[\text{Ox}_1][\text{Red}_2]}$$

where, the terms within [] represent the equilibrium concentrations of the respective species in the solution. The overall redox reaction involves two redox systems, both involving the same number (n) of electrons (say).



$$E_1 = E_1^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}_1]}{[\text{Red}_1]} \quad (\text{at } 25^\circ\text{C})$$



$$E_2 = E_2^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}_2]}{[\text{Red}_2]} \quad (\text{at } 25^\circ\text{C}).$$

where, the term E_1 , $E_1^{\circ'}$, E_2 , $E_2^{\circ'}$ and the numerical factor 0.059 have their usual meanings. Thus, in the net reaction, the system-1 is the oxidant couple and the system-2 is the reductant couple. When the two redox systems react and an equilibrium is established, the electrode potentials of the two systems become equal, i.e.,

$$E_1 = E_2$$

$$\therefore E_1^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}_1]}{[\text{Red}_1]} = E_2^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}_2]}{[\text{Red}_2]}$$

$$\text{or, } (E_1^{\circ'} - E_2^{\circ'}) = \frac{0.059}{n} \log_{10} \frac{[\text{Ox}_2][\text{Red}_1]}{[\text{Ox}_1][\text{Red}_2]}$$

$$\text{or, } (E_1^{\circ'} - E_2^{\circ'}) = \frac{0.059}{n} \log_{10} K$$

$$\therefore \log_{10} K = \frac{n(E_1^{\circ'} - E_2^{\circ'})}{0.059}$$

$$\therefore K = 10^{n(E_1^{\circ'} - E_2^{\circ'})/0.059} = 10^{n\Delta E^{\circ'}/0.059}$$

where, $E_1^{\circ'}$ and $E_2^{\circ'}$ are the stoichiometric standard potentials of the oxidant and the reductant couples respectively.

For practical purpose, it is often useful to calculate the equilibrium constant (K) using the formal potentials (E_1^f and E_2^f) applying the relations of the types:

$$\log_{10} K = \frac{n(E_1^f - E_2^f)}{0.059} = \frac{n\Delta E^f}{0.059}$$

$$\therefore K = 10^{n(E_1^f - E_2^f)/0.059} = 10^{n\Delta E^f/0.059}$$

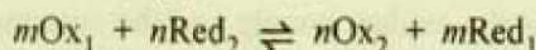
where, E_1^f and E_2^f are the formal potentials of the oxidant and the reductant couples respectively. The formal potentials (E_1^f, E_2^f) are defined in terms of analytical concentrations (c 's) of the components of the redox couples:

$$E_1 = E_1^f + \frac{0.059}{n} \log_{10} \frac{c_{\text{Ox}_1}}{c_{\text{Red}_1}}$$

$$E_2 = E_2^f + \frac{0.059}{m} \log_{10} \frac{c_{\text{Ox}_2}}{c_{\text{Red}_2}}$$

Thus, formal potentials (E^f) are the standard potentials when both the components, oxidant and the reductant, of a redox couple are at their analytical concentration of 1 mol.lit^{-1} , (i.e., $1M$).

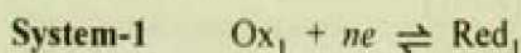
Equilibrium constant (K_{mn}) of a generalized redox reaction,



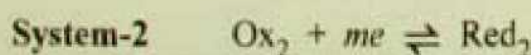
may be defined according to,

$$K_{mn} = \frac{[\text{Ox}_2]^n [\text{Red}_1]^m}{[\text{Ox}_1]^m [\text{Red}_2]^n}$$

The above overall redox reaction involves two redox systems, each involving different number of electrons:



$$E_1 = E_1^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}_1]}{[\text{Red}_1]} \quad (\text{at } 25^\circ\text{C})$$



$$E_2 = E_2^{\circ'} + \frac{0.059}{m} \log_{10} \frac{[\text{Ox}_2]}{[\text{Red}_2]} \quad (\text{at } 25^\circ\text{C})$$

At equilibrium, $E_1 = E_2$

$$\therefore E_1^{\circ'} + \frac{0.059}{n} \log_{10} \frac{[\text{Ox}_1]}{[\text{Red}_1]} = E_2^{\circ'} + \frac{0.059}{m} \log_{10} \frac{[\text{Ox}_2]}{[\text{Red}_2]}$$

Multiplying both sides of the equation with mn and simplifying one obtains,

$$mn(E_1^{\circ'} - E_2^{\circ'}) = 0.059 \log_{10} \frac{[\text{Ox}_2]^n [\text{Red}_1]^m}{[\text{Ox}_1]^m [\text{Red}_2]^n} = 0.059 \log_{10} K_{mn}$$

$$\therefore \log_{10} K_{mn} = \frac{mn(E_1^{\circ'} - E_2^{\circ'})}{0.059}$$

$$\text{or, } K_{mn} = 10^{mn(E_1^{\circ'} - E_2^{\circ'})/0.059} = 10^{mn\Delta E^{\circ'}/0.059}$$

For practical purpose, it is often convenient to calculate the equilibrium constant (K_{mn}) in terms of the formal potentials (E_1^f and E_2^f) using the relations,

$$\log K_{mn} = \frac{mn(E_1^f - E_2^f)}{0.059} = \frac{mn\Delta E^f}{0.059}$$

$$K_{mn} = 10^{mn(E_1^f - E_2^f)/0.059} = 10^{n\Delta E^f/0.059}$$

instead of the stoichiometric standard redox potentials ($E_1^{\circ'}$ and $E_2^{\circ'}$).

The magnitude of the equilibrium constant of a reaction directly gives the feasibility and also quantitateness of a reaction, although it says nothing about the speed of the reaction.

(i) Limiting values of equilibrium constants of redox reactions in aqueous solution

Equilibrium constant K_{mn} of a generalized redox reaction,



may be expressed in terms of the formal potentials E_1^f and E_2^f of the two interacting redox couples, Ox_1/Red_1 and Ox_2/Red_2 respectively according to the relation,

$$K_{mn} = 10^{mn(E_1^f - E_2^f)/0.059} = 10^{n\Delta E^f/0.059}$$

For a simple system with $m = n = 1$, the equilibrium constant K is given by

$$K = 10^{(E_1^f - E_2^f)/0.059} = 10^{\Delta E^f/0.059}$$

Most redox couples existing in aqueous media (*cf.* redox stability field of water, Fig 2.3) have their E^f values within the range: +1.23V in acid medium ($[\text{H}^+] = 1M$) to -0.828 V in basic medium ($[\text{OH}^-] = 1M$). Thus, the differences between the formal potential values of the interacting redox couples will be as narrow as around 2V. Considering an extended range of potential difference from +2V to -2V, the equilibrium constant (K) for one electron ($n = 1$) transfer redox reactions in aqueous solution will range from $\sim 10^{34}$ to $\sim 10^{-34}$.

$\Delta E^f(\text{V})$	+2	+1	0	-1	-2
K	10^{34}	10^{17}	1	10^{-17}	10^{-34}

(ii) Minimum value of K for quantitateness (i.e. feasibility) of redox reactions

Consider the generalized reversible redox reaction,



If the reaction is to proceed up to 99.9% at equilibrium, then the value of the equilibrium constant, K, should be,

$$K = \frac{[\text{Ox}_2]^n [\text{Red}_1]^m}{[\text{Ox}_1]^m [\text{Red}_2]^n} = \frac{(99.9)^n \times (99.9)^m}{(0.1)^m \times (0.1)^n} \approx \frac{(100)^n \times (100)^m}{(0.1)^m \times (0.1)^n} = 10^{3(m+n)}$$

The difference in the formal potentials $(E_1^f - E_2^f = \Delta E^f)$ of the two redox couples, Ox_1/Red_1 and Ox_2/Red_2 is related to the equilibrium constant K according to,

$$(E_1^f - E_2^f) = \Delta E^f = \left(\frac{0.059 \log K_{\text{eq}}}{mn} \right) \text{V}$$

For a system with $m = n = 1$, $K = 10^6 \therefore \log K = 6$

$$\therefore \Delta E^f = \left(\frac{0.059 \times 6}{1} \right) \text{V} = 0.354 \text{ V}$$

For a system with $m = 2$, $n = 1$ $K = 10^9 \therefore \log K = 9$

$$\therefore \Delta E^f = \frac{0.059 \times 9}{2.1} \text{V} = 0.266 \text{ V}$$

For system with $m = 5$, $n = 1$ $K = 10^{18} \therefore \log K = 18$

$$\therefore \Delta E^f = \frac{0.059 \times 18}{5.1} \text{V} = 0.212 \text{ V}$$

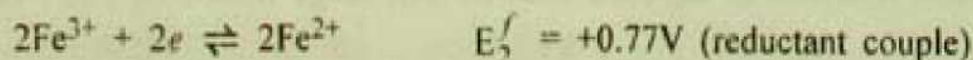
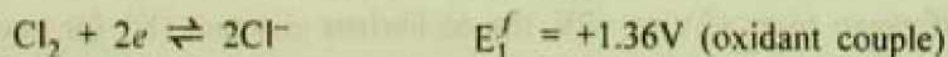
Examples (2.40)

(1) Formal potentials of the redox couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Cl}_2/2\text{Cl}^-$ at 25°C are + 0.77V and +1.36 V respectively. What redox reaction do you expect between these two couples? Is the reaction feasible?

Since $E^f(\text{Cl}_2/2\text{Cl}^-) > E^f(\text{Fe}^{3+}/\text{Fe}^{2+})$, the oxidant (Cl_2) of the $\text{Cl}_2/2\text{Cl}^-$ couple should oxidize the reductant (Fe^{2+}) of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple and the overall reaction should be,



Number of electrons transferred in this reaction is 2,



The equilibrium constant (K) of the reaction may be defined as,

$$K = \frac{[\text{Fe}^{3+}]^2 [\text{Cl}^-]^2}{[\text{Cl}_2] [\text{Fe}^{2+}]^2}$$

A tentative estimate of K may be obtained from the formal potentials (E^f) of the two interacting redox couples:

$$\log_{10} K = \frac{2[E^f(\text{Cl}_2 / 2\text{Cl}^-) - E^f(\text{Fe}^{3+} / \text{Fe}^{2+})]}{0.059}$$

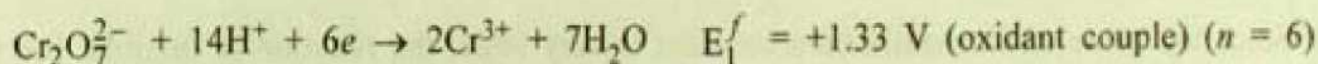
$$= \frac{2[1.36 - 0.77]}{0.059} = 20$$

$$\therefore K = 10^{20}$$

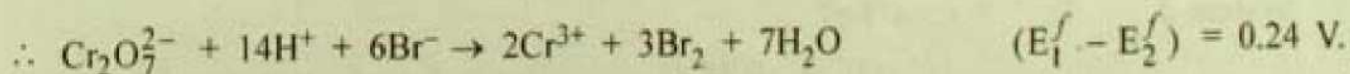
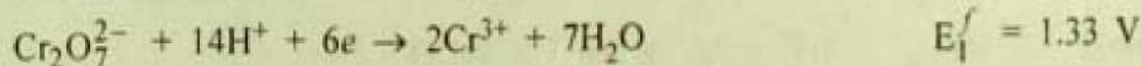
Since, K is very large, the reaction is feasible and goes almost to completion. In qualitative inorganic analysis Fe^{2+} ion may be oxidized to Fe^{3+} ion by Cl_2 -water. Addition of NH_4SCN to a solution of ferrous salt does not produce any red colour. If a few drops of Cl_2 - water is added to the solution of ferrous salt, Fe^{2+} is oxidized to Fe^{3+} . After boiling off the excess Cl_2 from the solution, if a few drops of NH_4SCN is added, a blood red colouration due to the ferric complex, $\text{Fe}(\text{SCN})^{2+}$ is produced.

(2) Formal potentials of $\text{Cr}_2\text{O}_7^{2-} / 2\text{Cr}^{3+}$ and $\text{Br}_2 / 2\text{Br}^-$ couples in 1 (M) acid medium at 25°C are 1.33 V and 1.09 V respectively. Test the feasibility of oxidation of Br^- by $\text{Cr}_2\text{O}_7^{2-}$ ion under this condition.

The two half-cell reactions are:



Atomically and ionically balanced equation of the overall reaction is obtained by multiplying the $\text{Br}_2 / 2\text{Br}^-$ half-cell reaction with 3 and adding with the half-cell reaction of $\text{Cr}_2\text{O}_7^{2-} / 2\text{Cr}^{3+}$ couple in the manner, so that the number of electrons cancel out from both sides of the overall equation:



Note

(i) E^f for the $2\text{Br}^- / \text{Br}_2$ oxidation is the negative ($-$) value of the E^f of $\text{Br}_2 / 2\text{Br}^-$ redox couple.

(ii) E^f values are not multiplied in balancing the chemical equation of redox reactions, since electrical potential is an intensive property, which does not depend upon the amount of the substances.

Now,

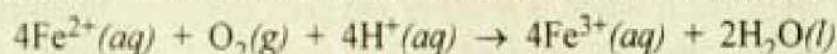
$$\log_{10} K = \frac{mn[E_1^f - E_2^f]}{0.059}$$

$$= \frac{(1)(6)[1.33 - 1.09]}{0.059} = \frac{(6)(0.24)}{0.059} \approx \frac{(6)(0.24)}{0.06} \approx 24$$

$$\therefore K \approx 10^{24}$$

Since, K is very large, the reaction is feasible.

(3) Aerial oxidation of ferrous salts in acidic medium may be represented by the reaction,



How far is this reaction feasible? [Given: formal potentials of $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{O}_2/2\text{H}_2\text{O}$ couples in 1 (M) acid medium at 25°C are: +0.77V and + 1.23V respectively).



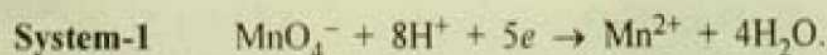
$$\log_{10} K = \frac{mn[E_1^f - E_2^f]}{0.059} = \frac{(1)(4)[1.23 - 0.77]}{0.059} = 31.2$$

$$\therefore K \approx 10^{31.2} \approx 1.58 \times 10^{31}$$

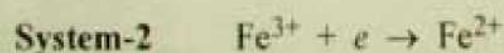
Since the value of the equilibrium constant is very large, the reaction is feasible. But the reaction is extremely slow because of high energy barrier to reduction of O_2 molecule which is a biradical. In fact, solution of ferrous salts in acid medium are stable to aerial oxidation and may be prepared and preserved in the laboratory without much precaution.

(4) Calculate the equilibrium constant of the reaction for oxidation of Fe^{2+} ion to Fe^{3+} ion by MnO_4^- ion in 1(M) acid medium. [Given : E^f values of $\text{MnO}_4^-/\text{Mn}^{2+}$ and $\text{Fe}^{3+}/\text{Fe}^{2+}$ couples in 1(M) acid medium at 25°C are +1.51 V and + 0.77 V. respectively.]

The two redox couples are:



$$E_1^f = 1.51\text{V}, \quad n = 5 \text{ (oxidant couple)}$$



$$E^f = +0.77 \text{ V}, \quad m = 1 \text{ (reductant couple)}$$

The overall reaction is,



The equilibrium constant, $K = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$

In terms of formal potentials,

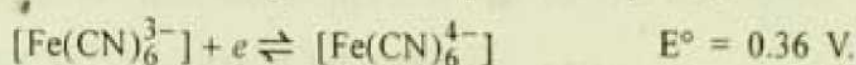
$$K = 10^{mnf(E_1^f - E_2^f)/0.059}$$

$$= 10^{(1)(5)(1.51 - 0.77)/0.059} = 10^{62.7} = 5.15 \times 10^{62}$$

The reaction goes almost to completion, since K is very large.

(h) Variation of Formal Potentials as a Function of pH

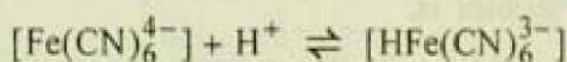
Formal potential of the ferricyanide-ferrocyanide redox couple shows wide variation with pH. The half-reaction for the ferricyanide-ferrocyanide couple is,



The Nernst equation for this couple, using the formal potential at 25°C may be written as,

$$E = E^f_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]} + 0.059 \log_{10} \frac{C_{[\text{Fe}(\text{CN})_6^{3-}]}}{C_{[\text{Fe}(\text{CN})_6^{4-}]}}$$

where, $C_{[\text{Fe}(\text{CN})_6^{4-}]}$ and $C_{[\text{Fe}(\text{CN})_6^{3-}]}$ are the analytical concentrations of $[\text{Fe}(\text{CN})_6^{4-}]$ and $[\text{Fe}(\text{CN})_6^{3-}]$ ions. In acidic solution $[\text{Fe}(\text{CN})_6^{4-}]$ ion tends to be associated with protons :



$$K_1^H = \frac{[\text{H}^+][\text{Fe}(\text{CN})_6^{4-}]}{[\text{HFe}(\text{CN})_6^{3-}]} = 5 \times 10^{-5} \quad (25^\circ \text{C})$$

$$\therefore [\text{HFe}(\text{CN})_6^{3-}] = \frac{[\text{H}^+]}{K_1^H} [\text{Fe}(\text{CN})_6^{4-}]$$



$$K_2^H = \frac{[\text{H}^+][\text{HFe}(\text{CN})_6^{3-}]}{[\text{H}_2\text{Fe}(\text{CN})_6^{2-}]} = 1 \times 10^{-3} \quad (25^\circ \text{C})$$

$$\therefore [\text{H}_2\text{Fe}(\text{CN})_6^{2-}] = \frac{[\text{H}^+]}{K_2^H} [\text{HFe}(\text{CN})_6^{3-}] = \frac{[\text{H}^+]^2}{K_1^H K_2^H} [\text{Fe}(\text{CN})_6^{4-}]$$

Since $C_{[\text{Fe}(\text{CN})_6^{4-}]}$ is the total analytical concentration of ferrocyanide ion, so, mass balance equation for the ferrocyanide species in acid medium will be,

$$\begin{aligned} C_{[\text{Fe}(\text{CN})_6^{4-}]} &= [\text{Fe}(\text{CN})_6^{4-}] + [\text{HFe}(\text{CN})_6^{3-}] + [\text{H}_2\text{Fe}(\text{CN})_6^{2-}] \\ &= [\text{Fe}(\text{CN})_6^{4-}] \left(1 + \frac{[\text{H}^+]}{K_1^{\text{H}}} + \frac{[\text{H}^+]^2}{K_1^{\text{H}} K_2^{\text{H}}} \right) \\ &= [\text{Fe}(\text{CN})_6^{4-}] a \\ \therefore [\text{Fe}(\text{CN})_6^{4-}] &= \frac{C_{[\text{Fe}(\text{CN})_6^{4-}]}}{a} \end{aligned}$$

$$\text{where, } a = 1 + \frac{[\text{H}^+]}{K_1^{\text{H}}} + \frac{[\text{H}^+]^2}{K_1^{\text{H}} K_2^{\text{H}}}$$

The term, a , represents the pH dependence of concentrations of various ferrocyanide species.

Because of smaller anionic charge, proton affinity of ferricyanide ion is much lower than that of ferrocyanide ion. As such, the equilibrium concentration of ferricyanide ion in dilute acid medium may be assumed to be equal to its analytical concentration, i.e.,

$$[\text{Fe}(\text{CN})_6^{3-}] \approx C_{[\text{Fe}(\text{CN})_6^{3-}]}$$

Nernst equation for the ferricyanide-ferrocyanide couple involving the equilibrium concentrations of the oxidant and reductant species is,

$$E = E_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]}^{\circ} + 0.059 \log_{10} \frac{[\text{Fe}(\text{CN})_6^{3-}]}{[\text{Fe}(\text{CN})_6^{4-}]} \quad (\text{at } 25^\circ\text{C})$$

Substituting the above values of the equilibrium concentrations of $[\text{Fe}(\text{CN})_6^{3-}]$ and $[\text{Fe}(\text{CN})_6^{4-}]$ ions in the Nernst equation, one obtains,

$$\begin{aligned} \therefore E &\approx E_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]}^{\circ} + 0.059 \log_{10} \frac{C_{[\text{Fe}(\text{CN})_6^{3-}]}}{C_{[\text{Fe}(\text{CN})_6^{4-}]} / a} \\ &= \left\{ E_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]}^{\circ} + 0.059 \log_{10} a \right\} + 0.059 \log \frac{C_{[\text{Fe}(\text{CN})_6^{3-}]}}{C_{[\text{Fe}(\text{CN})_6^{4-}]}} \\ &= E_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]}^f + 0.059 \log \frac{C_{[\text{Fe}(\text{CN})_6^{3-}]}}{C_{[\text{Fe}(\text{CN})_6^{4-}]}} \end{aligned}$$

where, $E^f_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]} = E^{\circ}_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]} + 0.059 \log a$

$$\approx E^{\circ}_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]} + 0.059 \log a$$

$$\approx (0.36 + 0.059 \log a) \text{ V at } 25^{\circ} \text{ C}$$

in dilute solution. Here, $E^f_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]}$ is the formal potential of the $[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$ redox couple.

Now the pH dependence parameter 'a' at different pH values may be calculated using the ionization constants of $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ and $\text{HFe}(\text{CN})_6^{3-}$ ions and pH of the solution. Substituting the value of log a in the above equation we obtain the formal potentials of the $[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$ couple at different pH.

$$\therefore K_1^{\text{H}} = 5 \times 10^{-5} \quad \therefore pK_1^{\text{H}} = 4.3$$

$$\therefore K_2^{\text{H}} = 1 \times 10^{-3} \quad \therefore pK_2^{\text{H}} = 3.0, \quad \therefore pK_1^{\text{H}} + pK_2^{\text{H}} = 7.3$$

Now, $\frac{[\text{H}^+]}{K_1^{\text{H}}} = \text{Inverse log}(pK_1^{\text{H}} - \text{pH}) = \text{Inv.log}(4.3 - \text{pH})$

$$\frac{[\text{H}^+]^2}{K_1^{\text{H}} K_2^{\text{H}}} = \text{Inverse log}(pK_1^{\text{H}} + pK_2^{\text{H}} - 2\text{pH}) = \text{Inv.log}(7.3 - 2\text{pH})$$

Calculated values of log a and $E^f_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]}$ at some specified pH values are

listed below:

pH	:	0	1	2	3	4	6	8	10
log a	:	7.3	5.3	3.3	1.6	0.5	-0.01	-0	-0
$E^f_{[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]} \text{ (V)}$	:	0.79	0.67	0.55	0.46	0.39	0.36	0.36	0.36

It is seen that the ferricyanide-ferrocyanide couple becomes stronger oxidant in acidic solution and serves as a mild oxidant or almost as a reductant in neutral or alkaline medium.

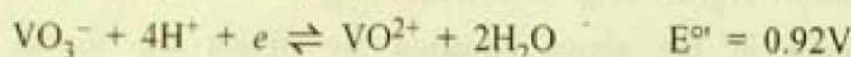
In the pH range 0 – 8, the redox potential of the $\text{I}_2/2\text{I}^-$ couple ($E^{\circ} = 0.53\text{V}$) is independent of pH of the solution. The formal potentials of $[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$ couple above pH 2 are lower than the E° of $\text{I}_2/2\text{I}^-$ couple. But at pH less than 2, the formal potentials of $[\text{Fe}(\text{CN})_6^{3-}]/[\text{Fe}(\text{CN})_6^{4-}]$ couple fairly exceed the E° value of $\text{I}_2/2\text{I}^-$ couple, and as such,

$[\text{Fe}(\text{CN})_6]^{3-}$ ion oxidizes I^- to liberate I_2 in acid medium. Thus, if both I^- and $[\text{Fe}(\text{CN})_6]^{3-}$ radicals are present in a sample, I_2 may be liberated if the sample solution is rendered strongly acidic or the solid sample is treated with acid, since ferricyanide ion is always associated with its conjugate reductant, ferrocyanide ion, in whatever small amounts.

pH dependence of redox potential is particularly important for the redox couples involving oxocations or oxoanions, in which the oxidant and the reductant components contain different number of oxygen atoms or the oxidant component contains one or more O-atoms but the reductant component does not contain any O-atom.

Examples (2.41)

(1) $\text{VO}_3^-, \text{H}^+/\text{VO}^{2+}$ Couple*



$$E = E^\circ + 0.059 \log_{10} \frac{[\text{VO}_3^-][\text{H}^+]^4}{[\text{VO}^{2+}]}$$

$$E = E^\circ + 0.059 \log_{10} [\text{H}^+]^4 + 0.059 \log \frac{[\text{VO}_3^-]}{[\text{VO}^{2+}]}$$

$$\therefore E = E^f + 0.059 \log \frac{C_{\text{VO}_3^-}}{C_{\text{VO}^{2+}}}$$

For a system in which $C_{\text{VO}_3^-} = C_{\text{VO}^{2+}}$

$$E = E^f = (E^\circ - 0.059 \times 4 \text{ } p[\text{H}])\text{V} = (E^\circ - 0.236 \text{ } pH)\text{V} \\ \approx (E^\circ - 0.236 \text{ } p[\text{H}])\text{V}$$

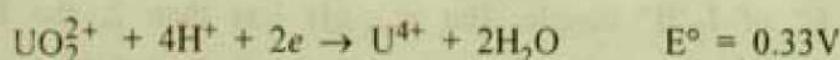
in dilute solution.

Taking $E^\circ(\text{VO}_3^-, \text{H}^+/\text{VO}^{2+}) = 0.92\text{V}$, the calculated formal potentials of the couple at some specified pH values are listed below:

$p[\text{H}]$	:	0	1	2	4	6
$E_{\text{VO}_3^-/\text{VO}^{2+}}^f (\text{V})$	:	0.92	0.684	0.448	-0.024	-0.496

Thus, the $\text{VO}_3^-, \text{H}^+/\text{VO}^{2+}$ system becomes more and more reducing in nature with increase of pH.

(2) $\text{UO}_2^{2+}, \text{H}^+/\text{U}^{4+}$ Couple*



* Rare elements

The Nernst equation for the couple is,

$$E = E^{\circ'} + \frac{0.059}{2} \log \frac{[\text{UO}_2^{2+}][\text{H}^+]^4}{[\text{U}^{4+}]}$$

$$E = E^{\circ'} + \frac{0.059}{2} \times 4 \log[\text{H}^+] + \frac{0.059}{2} \log \frac{[\text{UO}_2^{2+}]}{[\text{U}^{4+}]}$$

$$= E^{\circ'} - 0.118 \, p[\text{H}] + 0.0295 \log \frac{[\text{UO}_2^{2+}]}{[\text{U}^{4+}]}$$

$$= E^f + 0.0295 \log \frac{C_{\text{UO}_2^{2+}}}{C_{\text{U}^{4+}}}$$

For a system in which $C_{\text{UO}_2^{2+}} = C_{\text{U}^{4+}}$

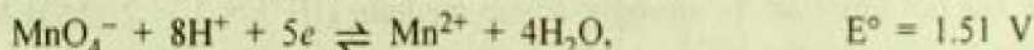
$$E = E^f = E^{\circ'} - 0.118 \, p[\text{H}] \approx E^{\circ} - 0.118 \, pH$$

Calculated formal potentials of UO_2^{2+} , $\text{H}^+ / \text{U}^{4+}$ couple at some specified $p\text{H}$ are given below:

$p[\text{H}]$	:	0	1	2	4	6
$E^f \text{UO}_2^{2+} / \text{U}^{4+} (\text{V})$	:	0.33	0.212	0.094	-0.142	-0.378

(3) MnO_4^- , $\text{H}^+/\text{Mn}^{2+}$ Couple

The half-cell reaction of the $(\text{MnO}_4^-, \text{H}^+/\text{Mn}^{2+})$ couple in acid medium is,



Assuming that the reaction is rapid and reversible and no intermediate oxidation state of Mn between M^{VII} and Mn^{II} are stable, the Nernst equation for the couple may be written as,

$$E = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ'} + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]}$$

$$= E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ'} + \frac{0.059}{5} \times 8 \log[\text{H}^+] + \frac{0.059}{5} \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

$$= E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ'} - 0.0944 \, p[\text{H}] + 0.0118 \log \frac{[\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

$$= E_{\text{MnO}_4^-/\text{Mn}^{2+}}^f + 0.0118 \log \frac{C_{\text{MnO}_4^-}}{C_{\text{Mn}^{2+}}}$$

where,
$$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^f = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} - 0.0944 p[\text{H}]$$

$$\approx E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} + 0.0944 \log C_{\text{H}^+}$$

For a system in which $C_{\text{MnO}_4^-} = C_{\text{Mn}^{2+}}$

$$E = E_{\text{MnO}_4^-/\text{Mn}^{2+}}^f$$

The $E_{\text{MnO}_4^-/\text{Mn}^{2+}}^f$ values at different H^+ ion concentrations show how the oxidizing power of MnO_4^- ion is decreased on lowering the H^+ ion concentration of the solution.

$C_{\text{H}^+} (M)$	2	1	0.5	0.1	0.01	10^{-4}		
$p[\text{H}]$	...	...	...	1	2	4	6	7
$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^f (V)$	1.54	1.51	1.48	1.42	1.32	1.13	0.94	0.85

Such a wide variation of formal potential provides scope for selective oxidation of individual components of a mixture of oxidizable substances. As for example, the E° values of the halogen/halide couples are :

	$\text{Cl}_2/2\text{Cl}^-$	$\text{Br}_2/2\text{Br}^-$	$\text{I}_2/2\text{I}^-$
$E^\circ(V) :$	1.36	1.09	0.53

Thus, in neutral solution ($p\text{H}$ 6-7), MnO_4^- can oxidize iodide to liberate iodine, but not bromide or chloride. Around $p\text{H}$ 2-3 (acetic acid medium) it can oxidize both bromide and iodide but not chloride. In strongly acidic medium ($[\text{H}^+] = 1 \sim 2 (M)$) MnO_4^- can oxidize chloride to liberate chlorine.

(4) $\text{Cr}_2\text{O}_7^{2-}, \text{H}^+/2\text{Cr}^{3+}$ Couple

Considering the half-cell reaction,



as rapid and reversible, the Nernst equation for the $\text{Cr}_2\text{O}_7^{2-}, \text{H}^+/2\text{Cr}^{3+}$ couple may be written

$$E = E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^{\circ} + \frac{0.059}{6} \log_{10} \frac{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2}$$

$$= \left\{ E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^{\circ} + \frac{0.059}{6} \times 14 \log_{10} [\text{H}^+] \right\} + \frac{0.059}{6} \log_{10} \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]^2}$$

$$\therefore E = E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^f + \frac{0.059}{6} \log_{10} \frac{C_{\text{Cr}_2\text{O}_7^{2-}}}{C_{\text{Cr}^{3+}}^2}$$

For a half-cell consisting of $C_{\text{Cr}_2\text{O}_7^{2-}} = 1 (M)$, $C_{\text{Cr}^{3+}} = 1 (M)$,

$$E = E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^f$$

$$\text{where, } E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^f = \left\{ E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^{\circ} + \frac{0.059}{6} \times 14 \log C_{\text{H}^+} \right\}$$

= Formal potential

In dilute solution,

$$E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^f \approx E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^{\circ} + \frac{0.059}{6} \cdot 14 \log_{10} C_{\text{H}^+}$$

$$= E_{\text{Cr}_2\text{O}_7^{2-}/2\text{Cr}^{3+}}^f + 0.138 \log_{10} C_{\text{H}^+}$$

$$= (1.33 + 0.138 \log C_{\text{H}^+}) \text{V}$$

$$\approx (1.33 - 0.138 p[\text{H}]) \text{V}$$

Calculated formal potentials of the $\text{Cr}_2\text{O}_7^{2-}$, $\text{H}^+ / 2\text{Cr}^{3+}$ couple at some specified H^+ ion concentrations and $p[\text{H}]$ values (neglecting the acid-base equilibrium):

$\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^- \rightleftharpoons 2\text{H}^+ + 2\text{CrO}_4^{2-}$ ($p. 420$) are listed below.

$C_{\text{H}^+} (M)$: 2 1 0.5 0.1 0.01 10^{-3}

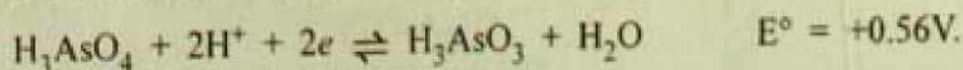
$\sim p[\text{H}]$: 1 2 3 5 7

$E^f (\text{Cr}_2\text{O}_7^{2-} / 2\text{Cr}^{3+}), (\text{V})$: 1.37 1.33 1.29 1.19 1.05 0.92 0.64 0.36

Thus, $\text{Cr}_2\text{O}_7^{2-}$ can not oxidize iodide in neutral solution ($p\text{H } 7$) but it can do so in acidic medium. In weakly acidic solution $C_{\text{H}^+} > 0.1 (M)$ it can oxidize both bromide and iodide. It can oxidize even chloride in strongly acidic medium (*cf.* E° values of halogen/halide couples given in Example - 3) above.

(5) $\text{H}_3\text{AsO}_4/\text{H}_3\text{AsO}_3$ Couple

The half-cell reaction for the As(V)/As (III) redox couple is



The Nernst equation for the couple may be written as,

$$\begin{aligned}
 E &= E^{\circ'} + \frac{0.059}{2} \log_{10} \frac{[\text{H}_3\text{AsO}_4][\text{H}^+]^2}{[\text{H}_3\text{AsO}_3]} \quad (\text{at } 25^\circ\text{C}) \\
 &= E^{\circ'} + 0.059 \log_{10}[\text{H}^+] + 0.0295 \log_{10} \frac{[\text{H}_3\text{AsO}_4]}{[\text{H}_3\text{AsO}_3]} \\
 &= E^{\circ'} - 0.059 p[\text{H}] + 0.0295 \log_{10} \frac{[\text{H}_3\text{AsO}_4]}{[\text{H}_3\text{AsO}_3]} \\
 &\approx E^f + 0.0295 \log_{10} \frac{C_{\text{H}_3\text{AsO}_4}}{C_{\text{H}_3\text{AsO}_3}}
 \end{aligned}$$

where, E^f is the apparent formal potential, assuming no deprotonation of H_3AsO_4 and H_3AsO_3 .

But both H_3AsO_4 and H_3AsO_3 are weak acids. In the working $p[\text{H}]$ range, H_3AsO_4 ionizes as a triprotic acid, whereas, H_3AsO_3 ionizes as a monoprotic acid. The pK^H values at 25°C are:

H_3AsO_4			H_3AsO_3
pK_3^H	pK_2^H	pK_1^H	pK^H
2.25	6.77	11.40	9.22

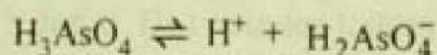
Therefore, in aqueous solution the mass balance equations of H_3AsO_4 and H_3AsO_3 will be,

$$C_{\text{H}_3\text{AsO}_4} = [\text{H}_3\text{AsO}_4] + [\text{H}_2\text{AsO}_4^-] + [\text{HAsO}_4^{2-}] + [\text{AsO}_4^{3-}]$$

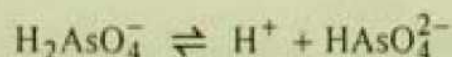
$$C_{\text{H}_3\text{AsO}_3} = [\text{H}_3\text{AsO}_3] + [\text{H}_2\text{AsO}_3^-]$$

where, $C_{\text{H}_3\text{AsO}_4}$ and $C_{\text{H}_3\text{AsO}_3}$ are the analytical concentrations of H_3AsO_4 and H_3AsO_3 respectively.

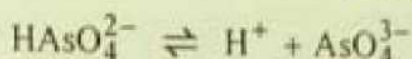
Stepwise deprotonation constants of H_3AsO_4 are defined according to,



$$K_3^H = \frac{[\text{H}^+][\text{H}_2\text{AsO}_4^-]}{[\text{H}_3\text{AsO}_4]} = 5.6 \times 10^{-3} \quad (25^\circ\text{C})$$



$$K_2^H = \frac{[\text{H}^+][\text{HAsO}_4^{2-}]}{[\text{H}_2\text{AsO}_4^-]} = 1.7 \times 10^{-7} \quad (25^\circ\text{C})$$



$$K_1^H = \frac{[\text{H}^+][\text{AsO}_4^{3-}]}{[\text{HAsO}_4^{2-}]} = 4 \times 10^{-12} \quad (25^\circ\text{C})$$

As the magnitude of the deprotonation constants are all low, the major As (V) containing species in acidic to neutral solution will be the H_3AsO_4 (major), H_2AsO_4^- (minor), HAsO_4^{2-} and AsO_4^{3-} (only traces). Therefore, it will be convenient to express the equilibrium concentrations of deprotonated As(V) species in terms of the major protonated species H_3AsO_4 . For similar reason, the equilibrium concentration of H_2AsO_3^- may be expressed in terms of that of H_3AsO_3 . Thus,

$$\begin{aligned} C_{\text{H}_3\text{AsO}_4} &= [\text{H}_3\text{AsO}_4] \left(1 + \frac{K_3^H}{[\text{H}^+]} + \frac{K_3^H K_2^H}{[\text{H}^+]^2} + \frac{K_3^H K_2^H K_1^H}{[\text{H}^+]^3} \right) \\ &= [\text{H}_3\text{AsO}_4](a) \end{aligned}$$

$$C_{\text{H}_3\text{AsO}_3} = [\text{H}_3\text{AsO}_3] \left(1 + \frac{K^H}{[\text{H}^+]} \right) = [\text{H}_3\text{AsO}_3](b)$$

where, 'a' and 'b' are the $p[\text{H}]$ dependence parameters of H_3AsO_4 and H_3AsO_3 respectively. 'a' and 'b' may be calculated for any $p[\text{H}]$ using the values of the deprotonation constants with the aid of the following relations:

$$\begin{aligned} a &= 1 + \frac{K_3^H}{[\text{H}^+]} + \frac{K_3^H K_2^H}{[\text{H}^+]^2} + \frac{K_3^H K_2^H K_1^H}{[\text{H}^+]^3} \\ b &= 1 + \frac{K^H}{[\text{H}^+]} \end{aligned}$$

The terms on the R.H.S. of these equations may be evaluated from the pK^H s and $p[\text{H}]$ values by the following procedure.

For H_3AsO_4 :

$$\frac{K_3^H}{[\text{H}^+]} = \text{Inverse log}[p[\text{H}] - pK_3^H] = \text{Inv. log}(p[\text{H}] - 2.25)$$

$$\begin{aligned} \frac{K_3^H K_2^H}{[\text{H}^+]^2} &= \text{Inverse log}[2p[\text{H}] - (pK_3^H + pK_2^H)] \\ &= \text{Inv. log}[2p[\text{H}] - (2.25 + 6.77)] \\ &= \text{Inv. log}(2p[\text{H}] - 9.02) \end{aligned}$$

$$\begin{aligned}\frac{K_3^H K_2^H K_1^H}{[H^+]^3} &= \text{Inverse log } [3p[H] - (pK_3^H + pK_2^H + pK_1^H)] \\ &= \text{Inv. log } [3p[H] - (2.25 + 6.77 + 11.40)] \\ &= \text{Inv. log } (3p[H] - 20.42)\end{aligned}$$

For H_3AsO_3 :

$$\frac{K^H}{[H^+]} = \text{Inverse log } (p[H] - pK^H) = \text{Inv. log}(p[H] - 9.22)$$

If the values of 'a' and 'b' at a particular $p[H]$ are known, one may calculate the equilibrium concentrations of H_3AsO_4 and H_3AsO_3 using the equations:

$$[H_3AsO_4] = \frac{C_{H_3AsO_4}}{a}$$

$$[H_3AsO_3] = \frac{C_{H_3AsO_3}}{b}$$

Substituting these values of $[H_3AsO_4]$ and $[H_3AsO_3]$ in the Nernst equation, one obtains the formal potential (E^f) of the As(V)/As(III) couple at that $p[H]$.

$$\begin{aligned}E &= E^\circ - 0.059p[H] + \frac{0.059}{2} \log_{10} \frac{C_{H_3AsO_4} / a}{C_{H_3AsO_3} / b} \\ &= \{E^\circ - 0.059p[H] + 0.0295 \log(b / a)\} + 0.0295 \log \frac{C_{H_3AsO_4}}{C_{H_3AsO_3}} \\ &= E^f + 0.0295 \log_{10} \frac{C_{H_3AsO_4}}{C_{H_3AsO_3}}\end{aligned}$$

where, E^f is the true formal potential taking account of deprotonation of H_3AsO_4 and H_3AsO_3 and it is given by the relation,

$$\begin{aligned}E^f &= E^\circ - 0.059p[H] + 0.0295 \log (b/a) \\ &\approx E^\circ - 0.059 p[H] + 0.0295 \log(b/a) \quad (\text{in dilute solution}) \\ \therefore E^f &= E^f + 0.0295 \log (b/a)\end{aligned}$$

E^f and E^f values of the As(V)/ As(III) couple at some specified H^+ ion concentrations and specified $p[H]$ values at 25°C , calculated using the $\log(b/a)$ values under these conditions, are listed below:

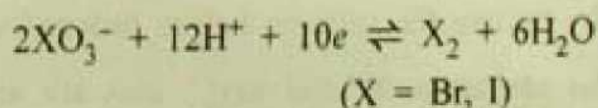
$C_{H^+} (M)$	$p[H]$	$\log(b/a)$	$E'(V)$	$E'(V)$
9	...	~ 0	0.62	0.62
6	...	~ 0	0.61	0.61
4	...	~ 0	0.60	0.60
2	...	~ 0	0.58	0.58
1	0	-0.0026	0.56	0.56
0.1	1	-0.024	0.501	0.500
0.01	2	-0.193	0.442	0.436
...	4	-1.76	0.324	0.272
...	6	-3.75	0.206	+0.096
...	7	-4.75	0.147	-0.007
...	8	-5.75	0.088	-0.082

The influence of deprotonation equilibria of H_3AsO_4 and H_3AsO_3 on the formal potentials of the As(V)/As(III) couple in acidic solution ($C_{H^+} \geq 1M$) is, however, quite small, since both are weak acids and are only poorly ionized in acidic and neutral $p[H]$. The major contributor to the variation of formal potentials is the variation of H^+ ion concentration (i.e. $p[H]$) of the solution, as $2H^+$ ions are involved in the half-cell reaction.

Such variation of formal potential (E') of H_3AsO_4/H_3AsO_3 system (calculated ignoring the deprotonation constants of H_3AsO_4 and H_3AsO_3) forms the basis of qualitative detection of arsenic by reversible redox reaction with $I_2/2I^-$ couple. If a neutral or faintly alkaline ($pH \leq 9$, sodium bicarbonate solution, $pH \sim 8.4$) solution of arsenite is treated with a blue starch-iodine solution, the blue colour is discharged as iodine oxidizes arsenite to arsenate [$E'(H_3AsO_4/H_3AsO_3)$ at $pH \sim 8.4$ is ≈ 0.09 V, whereas, $E^\circ(I_2/2I^-) = 0.53V$] and itself is reduced to iodide. On rendering the resulting colourless reaction mixture strongly acidic with HCl, the blue colour is restored as H_3AsO_4 oxidizes iodide to iodine and itself is reduced to H_3AsO_3 [$E'(H_3AsO_4/H_3AsO_3)$ at $9(M)$ HCl is $0.62V$, whereas, $E^\circ(I_2/2I^-) = 0.53V$]. On adding drops of concentrated solution of $NaHCO_3$, the blue colour is again discharged. The test may be carried out on a filter paper strip as well (cf. p. 269).

(6) $2BrO_3^-/Br_2$ and $2IO_3^-/I_2$ Couples

Assuming reversible half-cell reactions,



[$E^\circ(2BrO_3^-/Br_2) = 1.52V$ and $E^\circ(2IO_3^-/I_2) = 1.19V$], the Nernst equation for these couples may be written as,

$$E = E^{\circ'} + \frac{0.059}{10} \log_{10} [XO_3^-]^2 [H^+]^{12} \quad (\text{at } 25^{\circ}\text{C})$$

(since, $X_2 = Br_2$ (pure liquid), I_2 (pure solid))

Both $HBrO_3$ and HIO_3 are fairly strong acids and remain completely deprotonated as BrO_3^- and IO_3^- ions respectively in the entire working range of pH . So their unionized forms (HXO_3) are not involved in the redox equilibria.

$$\begin{aligned} \therefore E &= E^{\circ'} + \frac{0.059}{10} \log_{10} [H^+]^{12} + \frac{0.059}{10} \log_{10} [XO_3^-]^2 \\ &= (E^{\circ} - 0.0708 \, p[H]) + 0.0118 \log [XO_3^-] \\ &\approx E^f + 0.012 \log C_{XO_3^-} \end{aligned}$$

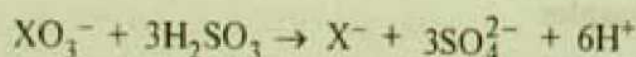
where, E^f is the formal potential and $C_{XO_3^-}$ is the analytical concentration of XO_3^- ion.

Here, $E^f \approx E^{\circ} - 0.071 \, p[H] \approx E^{\circ} - 0.071 \, p[H]$ (in dilute solution). Calculated values of formal potentials of $2BrO_3^-/Br_2$ and $2IO_3^-/I_2$ couples at some specified $p[H]$ values at 25°C are listed below:

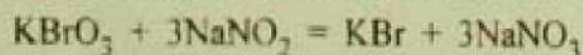
		$E^f = (E^{\circ} - 0.071 \, pH) \, V$							
$2XO_3^-/X_2$	$(E^{\circ}V)$	$p[H]$	0	1	2	4	6	7	8
$2BrO_3^-/Br_2$	1.52		1.52	1.45	1.38	1.24	1.10	1.02	0.95
$2IO_3^-/I_2$	1.19		1.19	1.12	1.05	0.91	0.77	0.69	0.62

Both the oxy anions, BrO_3^- and IO_3^- , are oxidizing agents and their oxidizing powers increase with decreasing $p[H]$. In neutral solution BrO_3^- can not oxidize bromide to bromine, [$E^{\circ}(Br_2/2Br^-) = 1.09V$] but iodate can oxidize iodide to iodine [$E^{\circ}(I_2/2I^-) = 0.53V$] even at neutral pH . Thus, if an inorganic mixture contains both BrO_3^- and Br^- , the test solution remains colourless so long it is neutral, but turns brown on acidification due to liberation of Br_2 . In qualitative inorganic analysis, many reactions require acidic test solutions, particularly in the tests for detection of anion radicals. If BrO_3^-/Br^- and/or IO_3^-/I^- mixtures are present in the sample, on acidification of the aqueous or sodium carbonate extract, the solution turns yellow brown due to liberation of Br_2 or, turns dark brown due to liberation of I_2 .

This is how BrO_3^-/Br^- and IO_3^-/I^- mixtures interfere in quantitative inorganic analysis. The problem may be easily overcome by reducing BrO_3^- and or IO_3^- by gentle boiling with a little SO_2 - water, which reduces these oxyanions to harmless halide ions:



Excess SO_2 has to be expelled by boiling the solution before proceeding to tests for the other radicals. Note that, through this operation, X^- and SO_4^{2-} ions are introduced into the solution. Bromate may also be reduced to bromide by digesting with sodium nitrite,



(i) Variation of Formal Potentials due to Complex Formation

(i) $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ Couples

Formal potentials of analytically important ferric-ferrous couple shows wide variation due to complex formation.

In acid medium ($[\text{H}^+] \geq 1\text{M}$), the ferric-ferrous couple is represented by the half cell reaction,



That is, the formal potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple under this condition is independent of H^+ ion concentration.

At lower acidity, however, the formal potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple depends upon pH of the solution, as the system is dominated by the hydroxo species, $\text{Fe}(\text{OH})_3$, $\text{Fe}(\text{OH})_2$ etc.

For simplicity, the variation of formal potentials of $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple in presence of complexing ligands may be considered in sufficiently acidic ($[\text{H}^+] \geq 1\text{M}$) medium, so that hydroxo species are not involved.

In the presence of a complexing ligand, say (L), which may form complexes with both Fe^{3+} ion (Fe^{III}) and Fe^{2+} ion (Fe^{II}), the formal potential depends upon the relative stabilities of the two complexes. If the ligand (L) forms only one complex with both Fe^{III} and Fe^{II} , according to the equilibria,



$$K_{\text{III}} = \frac{[\text{Fe}^{\text{III}}(\text{L})]}{[\text{Fe}^{\text{III}}][\text{L}]} \approx \frac{[\text{Fe}^{\text{III}}(\text{L})]}{C_{\text{Fe}^{\text{III}}}[\text{L}]}$$



$$K_{\text{II}} = \frac{[\text{Fe}^{\text{II}}(\text{L})]}{[\text{Fe}^{\text{II}}][\text{L}]} \approx \frac{[\text{Fe}^{\text{II}}(\text{L})]}{C_{\text{Fe}^{\text{II}}}[\text{L}]}$$

where, $C_{\text{Fe}^{\text{III}}}$ and $C_{\text{Fe}^{\text{II}}}$ represent the total analytical concentrations of Fe^{III} and Fe^{II} ions, K_{III} and K_{II} are the stoichiometric stability constants of the complexes $[\text{Fe}^{\text{III}}(\text{L})]$ and $[\text{Fe}^{\text{II}}(\text{L})]$ respectively. Charges are omitted for simplicity. The approximations, $[\text{Fe}^{\text{III}}] \approx C_{\text{Fe}^{\text{III}}}$ and $[\text{Fe}^{\text{II}}] \approx C_{\text{Fe}^{\text{II}}}$ are acceptable when the complexes $\text{Fe}^{\text{III}}(\text{L})$ and $\text{Fe}^{\text{II}}(\text{L})$ are not very stable, i.e., K_{III} and K_{II} are not very large. Now, in presence of the ligand (L) the total concentrations of Fe^{III} and Fe^{II} ions become,

$$C_{\text{Fe}^{\text{III}}} = [\text{Fe}^{\text{III}}(\text{L})]/([\text{L}].K_{\text{III}})$$

$$C_{\text{Fe}^{\text{II}}} = [\text{Fe}^{\text{II}}(\text{L})]/([\text{L}].K_{\text{II}})$$

The Nernst equation for the electrode potential of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple (at 25°C) may be written as,

$$E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}} = E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f + 0.059 \log_{10} \frac{C_{\text{Fe}^{\text{III}}}}{C_{\text{Fe}^{\text{II}}}}$$

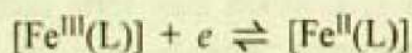
$$= E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f + 0.059 \log_{10} \frac{[\text{Fe}^{\text{III}}(\text{L})]K_{\text{II}}}{[\text{Fe}^{\text{II}}(\text{L})]K_{\text{III}}}$$

$$\therefore E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}} = \left(E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f + 0.059 \log_{10} \frac{K_{\text{II}}}{K_{\text{III}}} \right) + 0.059 \log \frac{[\text{Fe}^{\text{III}}(\text{L})]}{[\text{Fe}^{\text{II}}(\text{L})]}$$

which appears to be the Nernst equation,

$$E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}} = E_{[\text{Fe}^{\text{III}}(\text{L})]/[\text{Fe}^{\text{II}}(\text{L})]}^f + 0.059 \log \frac{[\text{Fe}^{\text{III}}(\text{L})]}{[\text{Fe}^{\text{II}}(\text{L})]}$$

for the complex redox couple,



where, $E_{[\text{Fe}^{\text{III}}(\text{L})]/[\text{Fe}^{\text{II}}(\text{L})]}^f = E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f + 0.059 \log \frac{K_{\text{II}}}{K_{\text{III}}}$

$E_{[\text{Fe}^{\text{III}}(\text{L})]/[\text{Fe}^{\text{II}}(\text{L})]}^f$ is the formal potential of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ system in presence of the complexing ligand (L).

Thus, the formal potential of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple, in presence of a complexing ligand (L) that forms complexes with both Fe^{III} and Fe^{II} ions, depends upon the ratio of the stability constants of the $[\text{Fe}^{\text{II}}(\text{L})]$ complex to that of the $[\text{Fe}^{\text{III}}(\text{L})]$ complex. If the Fe^{III} complex is more stable than the Fe^{II} complex ($K_{\text{III}} > K_{\text{II}}$), formal potential will decrease and if the Fe^{II} complex is more stable than the Fe^{III} complex, formal potential will increase:

$$\begin{array}{ll} K_{\text{III}} > K_{\text{II}}: & E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f < E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^{\circ} \\ K_{\text{III}} < K_{\text{II}}: & E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f > E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^{\circ} \end{array}$$

Examples (2.42)

(1) $[\text{Fe}^{\text{III}}(\text{phen})_3]^{3+} / [\text{Fe}^{\text{II}}(\text{phen})_2]^{2+}$ couple

In presence of 1,10-phenanthroline (phen), both Fe^{III} and Fe^{II} form 1:3 metal : ligand complexes:



$$K_{\text{III}} = \frac{[\text{Fe}^{\text{III}}(\text{phen})_3]}{[\text{Fe}^{\text{III}}][\text{phen}]^3} \approx \frac{[\text{Fe}^{\text{III}}(\text{phen})_3]}{C_{\text{Fe}^{\text{III}}}[\text{phen}]^3}$$

$$\therefore C_{\text{Fe}^{\text{III}}}^{\text{III}} = [\text{Fe}^{\text{III}}(\text{phen})_3] / (K_{\text{III}} \cdot [\text{phen}]^3)$$



$$K_{\text{II}} = \frac{[\text{Fe}^{\text{II}}(\text{phen})_3]}{[\text{Fe}^{\text{II}}][\text{phen}]^3} \approx \frac{[\text{Fe}^{\text{II}}(\text{phen})_3]}{C_{\text{Fe}^{\text{II}}}[\text{phen}]^3}$$

$$C_{\text{Fe}^{\text{II}}} = [\text{Fe}^{\text{II}}(\text{phen})_3]/(K_{\text{II}}[\text{phen}]^3)$$

(charges are omitted for simplicity)

$$\frac{C_{\text{Fe}^{\text{III}}}}{C_{\text{Fe}^{\text{II}}}} = \frac{K_{\text{II}}[\text{Fe}^{\text{III}}(\text{phen})_3]}{K_{\text{III}}[\text{Fe}^{\text{II}}(\text{phen})_3]}$$

The Nernst equation of the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple in terms of formal potential is,

$$E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}} = E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f + 0.059 \log_{10} \frac{C_{\text{Fe}^{\text{III}}}}{C_{\text{Fe}^{\text{II}}}}$$

This is now transformed to,

$$\begin{aligned} E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}} &= \left(E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f + 0.059 \log_{10} \frac{K_{\text{II}}}{K_{\text{III}}} \right) + 0.059 \log_{10} \frac{[\text{Fe}^{\text{III}}(\text{phen})_3]}{[\text{Fe}^{\text{II}}(\text{phen})_3]} \\ &= E_{\text{Fe}^{\text{III}}(\text{phen})_3/[\text{Fe}^{\text{II}}(\text{phen})_3]}^f + 0.059 \log_{10} \frac{[\text{Fe}^{\text{III}}(\text{phen})_3]}{[\text{Fe}^{\text{II}}(\text{phen})_3]} \end{aligned}$$

The above equation now corresponds to the complexed redox couple,



of which the formal potential is,

$$E_{[\text{Fe}^{\text{III}}(\text{phen})_3]/[\text{Fe}^{\text{II}}(\text{phen})_3]}^f = E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f + 0.059 \log_{10} \frac{K_{\text{II}}}{K_{\text{III}}}$$

In 1 (M) H_2SO_4 medium, $E_{\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}}^f = 0.68\text{V}$ and the ratio of the two stability constants is,

$$\frac{K_{\text{II}}}{K_{\text{III}}} = 2.8 \times 10^6$$

That is, the $[\text{Fe}^{\text{II}}(\text{phen})_3]$ complex is 2.8×10^6 times more stable than the $[\text{Fe}^{\text{III}}(\text{phen})_3]$ complex. Under this condition, the formal potential of the system will be,

$$\begin{aligned} E_{[\text{Fe}^{\text{III}}(\text{phen})_3]/[\text{Fe}^{\text{II}}(\text{phen})_3]}^f &= +0.68\text{V} + 0.059 \log 2.8 \times 10^6\text{V} \\ &= 1.06\text{V}. \end{aligned}$$

Thus, the formal potential is increased from 0.68V to 1.06 V in presence of the phen ligand, which forms more stable complex with Fe^{II} than with Fe^{III} .

(2) $[\text{Fe}(\text{CN})_6]^{3-} / [\text{Fe}(\text{CN})_6]^{4-}$ Couple

The cyanide (CN^-) ligand, on the other hand, stabilizes Fe^{III} state relative to Fe^{II} state. Comparison of the E° values of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ (+0.77V) and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} / [\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ (+0.365V) complex, gives us a tentative estimate of the stabilization of the Fe^{III} state relative to the Fe^{II} state by the CN^- ligand. For dilute solutions, ignoring the formation of hydroxo complexes by Fe^{III} and Fe^{II} ions and protonated forms of CN^- , $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ and $[\text{Fe}(\text{CN})_6]^{4-}$ ions, we can relate the stability constants K_{III} and K_{II} respectively of the $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ and $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ complexes with the E° values of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ and $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} / [\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ couples according to the relation:

$$E^\circ_{[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-} / [\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}} = E^\circ_{\text{Fe}^{\text{III}} / \text{Fe}^{\text{II}}} + 0.059 \log_{10} \frac{K_{\text{II}}}{K_{\text{III}}}$$

$$\therefore 0.365 = 0.77 + 0.059 \log \frac{K_{\text{II}}}{K_{\text{III}}}$$

This gives,

$$\frac{K_{\text{II}}}{K_{\text{III}}} \approx 1.37 \times 10^{-7}$$

i.e, $K_{\text{III}} = 7.3 \times 10^6 K_{\text{II}}$

which indicates the $[\text{Fe}^{\text{III}}(\text{CN})_6]^{3-}$ complex is 7.3×10^6 times more stable than the $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$ complex.

We can therefore, generalize the relation between the stability of complexes with the formal potentials according to the relation :

$$E^f_{\text{complexed couple}} = E^f_{\text{uncomplexed couple}} + \frac{0.059}{n} \log \frac{K_{\text{Red complex}}}{K_{\text{Ox complex}}}$$

$$\frac{K_{\text{Red complex}}}{K_{\text{Ox complex}}} = 10^{n(E^f_{\text{complexed couple}} - E^f_{\text{uncomplexed couple}})/0.059}$$

Examples (2.43)

(1) In a buffer solution of pH ~5, the formal potential of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple is +0.74V and that of $\text{Fe}^{\text{III}}(\text{EDTA})^- / \text{Fe}^{\text{II}}(\text{EDTA})^{2-}$ couple is +0.12V. Compare the stability of $\text{Fe}^{\text{III}}(\text{EDTA})^-$ complex relative to that of the $\text{Fe}^{\text{II}}(\text{EDTA})^{2-}$ complex under this condition.

Let, K_{III} = stability constant of $Fe^{III}(EDTA)^-$ complex,

K_{II} = stability constant of $Fe^{II}(EDTA)^{2-}$ complex.

The formal potentials of the complexed and uncomplexed redox couples are related according to,

$$E_{complexed\ couple}^f = E_{uncomplexed\ couple}^f + \frac{0.059}{n} \log \frac{K_{Red}}{K_{Ox}}$$

For the present redox couple $n = 1$, therefore,

$$0.12 = 0.74 + 0.059 \log \frac{K_{II}}{K_{III}}$$

$$\therefore \frac{K_{II}}{K_{III}} = 10^{(0.12-0.74)/0.059} = 3 \times 10^{-11}$$

$$\therefore K_{III} = 3.2 \times 10^{10} K_{II}$$

Thus, the $Fe^{III}(EDTA)^-$ complex is $\sim 3.2 \times 10^{10}$ times more stable than the $Fe^{II}(EDTA)^{2-}$ complex.

(2) Ratio of stability constant of $Fe^{III}F^{2+}$ complex to that of $Fe^{II}F^+$ complex is 10^5 . How will the formal potential of Fe^{III}/Fe^{II} couple change in presence of sufficient excess of fluoride ion in 1 (M) H_2SO_4 medium? (Given : $E_{Fe^{III}/Fe^{II}}^f = 0.68V$ in 1M H_2SO_4)

The formal potentials are related to the stability constants of the complexes according to,

$$E_{Fe^{III}F^{2+}/Fe^{II}F^+}^f = E_{Fe^{III}/Fe^{II}}^f + 0.059 \log \frac{K_{Fe^{II}F^+}}{K_{Fe^{III}F^{2+}}}$$

$$\text{Since, } \frac{K_{Fe^{III}F^{2+}}}{K_{Fe^{II}F^+}} = 10^5$$

$$\therefore E_{Fe^{III}F^{2+}/Fe^{II}F^+}^f = (0.68 + 0.059 \log 10^{-5})V = 0.385V$$

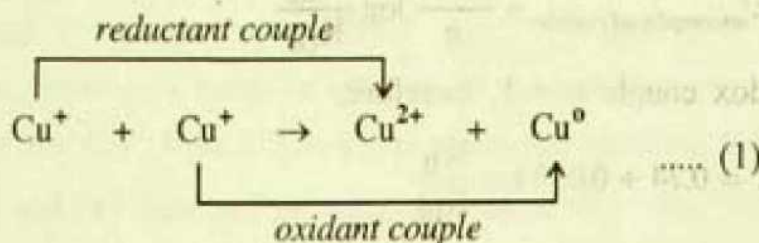
Therefore, the formal potential of the Fe^{III}/Fe^{II} couple will decrease significantly under the given condition.

(3) The ratio of stability constants of $Fe^{III}(HPO_4)^+$ and $Fe^{II}(HPO_4)$ complexes is $10^{4.2}$. What will be the formal potential of Fe^{III}/Fe^{II} couple in presence of sufficient excess of phosphoric acid in 1M H_2SO_4 medium, if the formal potential of the couple is 0.68V in absence of phosphoric acid?

$$\begin{aligned} E_{Fe^{III}(HPO_4)/Fe^{II}(HPO_4)}^f &= E_{Fe^{III}/Fe^{II}}^f + 0.059 \log \frac{K_{Fe^{II}(HPO_4)}}{K_{Fe^{III}(HPO_4)}} \\ &= 0.68 + 0.059 \log 10^{-4.2} \\ &= 0.43 V. \end{aligned}$$

(ii) $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ Couples

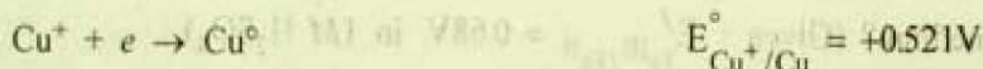
The effect of complex formation on the stability of various oxidation states of a metal is also evident from the variation of the tendency of Cu^+ ion to undergo disproportionation reaction in the absence and in the presence of a complexing ligand such as NH_3 . In absence of the ligand NH_3 , Cu^+ disproportionates according to,



The disproportionation equilibrium constant (K'_{120} , where the subscript 120 means oxidation state +1 disproportionates to +2 and 0 oxidation states, and the dash (') indicates concentration quotient) is defined as,

$$K'_{120} = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2}$$

The above overall reaction may be splitted into two half-reactions,



$$E_{\text{Cu}^+/\text{Cu}^0} = E^\circ_{\text{Cu}^+/\text{Cu}^0} + 0.059 \log[\text{Cu}^+]$$



$$E_{\text{Cu}^{2+}/\text{Cu}^+} = E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} + 0.059 \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]}$$

$$\therefore \text{At equilibrium, } E_{\text{Cu}^+/\text{Cu}^0} = E_{\text{Cu}^{2+}/\text{Cu}^+}$$

$$\therefore E^\circ_{\text{Cu}^+/\text{Cu}^0} + 0.059 \log[\text{Cu}^+] = E^\circ_{\text{Cu}^{2+}/\text{Cu}^+} + 0.059 \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]}$$

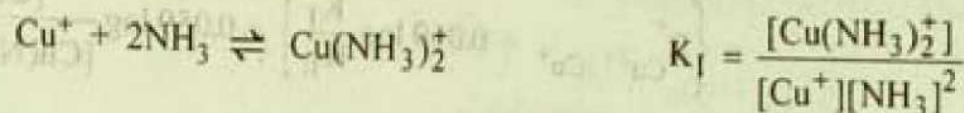
$$\therefore (E^\circ_{\text{Cu}^+/\text{Cu}^0} - E^\circ_{\text{Cu}^{2+}/\text{Cu}^+}) = 0.059 \log \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2} = 0.059 \log K'_{120}$$

$$\therefore K'_{120} = 10^{(E^\circ_{\text{Cu}^+/\text{Cu}^0} - E^\circ_{\text{Cu}^{2+}/\text{Cu}^+})/0.059}$$

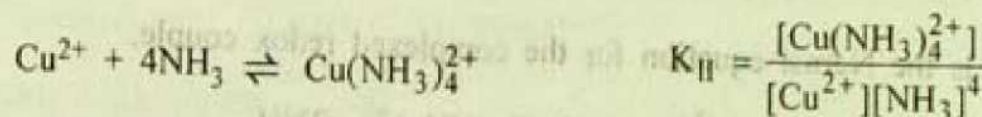
In dilute solution and in the absence of any supporting electrolyte, $K'_{120} \approx K^\circ_{120}$ (i.e the thermodynamic equilibrium constant), and $E^\circ \approx E^\circ$. Therefore,

$$\begin{aligned}
 K_{120}^{\circ} &= 10^{(E_{\text{Cu}^+/\text{Cu}^{\circ}}^{\circ} - E_{\text{Cu}^{2+}/\text{Cu}^+}^{\circ})/0.059} \\
 &= 10^{(0.521 - 0.153)/0.059} \\
 &= 10^{6.23} \approx 1.73 \times 10^6
 \end{aligned}$$

In presence of NH_3 ligand, both Cu^+ and Cu^{2+} ions form the corresponding ammine complexes according to,



$$\therefore [\text{Cu}^+] = \frac{[\text{Cu}(\text{NH}_3)_2^+]}{K_I[\text{NH}_3]^2}$$



$$\therefore [\text{Cu}^{2+}] = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{K_{II}[\text{NH}_3]^4}$$

Since the stability constants (K_I and K_{II}) of both the ammine complexes, $\text{Cu}(\text{NH}_3)_2^+$ and $\text{Cu}(\text{NH}_3)_4^{2+}$ are fairly large, so, in presence of NH_3 , the $\text{Cu}^+/\text{Cu}^{\circ}$ couple will be transformed to $\text{Cu}(\text{NH}_3)_2^+/\text{Cu}^{\circ}$ couple and the $\text{Cu}^{2+}/\text{Cu}^+$ couple will be transformed to $\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{NH}_3)_2^+$ couple. Redox potentials of these two new couples will be given by $E_{\text{Cu}(\text{NH}_3)_2^+/\text{Cu}^{\circ}}$

and $E_{\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{NH}_3)_2^+}$ respectively:

$$\begin{aligned}
 E_{\text{Cu}(\text{NH}_3)_2^+/\text{Cu}^{\circ}} &= E_{\text{Cu}^+/\text{Cu}^{\circ}}^{\circ} + 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_2^+]}{K_I[\text{NH}_3]^2} \\
 &= (E_{\text{Cu}^+/\text{Cu}^{\circ}}^{\circ} - 0.059 \log K_I) + 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_2^+]}{[\text{NH}_3]^2} \\
 &= E_{\text{Cu}(\text{NH}_3)_2^+/\text{Cu}^{\circ}}^{\circ} + 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_2^+]}{[\text{NH}_3]^2}
 \end{aligned}$$

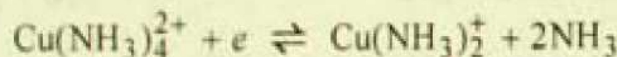
which is the Nernst equation for the complexed couple,



where, $E_{\text{Cu}(\text{NH}_3)_2^+/\text{Cu}^0}^\circ = E_{\text{Cu}^+/\text{Cu}}^\circ - 0.059 \log K_1$
 $= (0.521 - 0.059 \log 10^{10.8}) \text{V} \approx -0.12 \text{V}.$

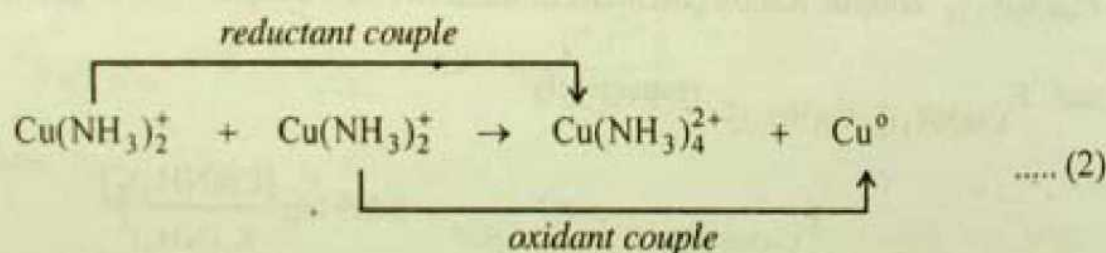
$$\begin{aligned}
 E_{\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{NH}_3)_2^+} &= E_{\text{Cu}^{2+}/\text{Cu}^+}^\circ + 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_4^{2+} / K_{II} \cdot [\text{NH}_3]^4]}{[\text{Cu}(\text{NH}_3)_2^+ / K_I [\text{NH}_3]^2]} \\
 &= \left\{ E_{\text{Cu}^{2+}/\text{Cu}^+}^\circ + 0.059 \log \frac{K_I}{K_{II}} \right\} + 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{NH}_3)_2^+][\text{NH}_3]^2} \\
 &= E_{\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{NH}_3)_2^+}^\circ + 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{NH}_3)_2^+][\text{NH}_3]^2}
 \end{aligned}$$

which is the Nernst equation for the complexed redox couple,



where, $E_{\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{NH}_3)_2^+}^\circ = E_{\text{Cu}^{2+}/\text{Cu}^+}^\circ + 0.059 \log \frac{K_I}{K_{II}}$
 $= \left(0.153 + 0.059 \log \frac{10^{10.8}}{10^{13.6}} \right) \text{V} \approx -0.01 \text{V}.$

Since both Cu^{2+} and Cu^+ ions exist as their ammine complexes in presence of NH_3 , the disproportionation equilibrium (1) is also transformed to,



and the disproportionation equilibrium constant (K_{120}) may be expressed as,

$$K_{120} = \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{NH}_3)_2^+]^2}$$

At the disproportionation equilibrium,

$$E_{\text{Cu}(\text{NH}_3)_2^+/\text{Cu}^0} = E_{\text{Cu}(\text{NH}_3)_4^{2+}/\text{Cu}(\text{NH}_3)_2^+}$$

$$\begin{aligned}
 \therefore E_{\text{Cu}(\text{NH}_3)_2^+/ \text{Cu}^0}^\circ + 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_2^{2+}]}{[\text{NH}_3]^2} \\
 &= E_{\text{Cu}(\text{NH}_3)_4^{2+}/ \text{Cu}(\text{NH}_3)_2^+}^\circ + 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{NH}_3)_2^+][\text{NH}_3]^2} \\
 \therefore E_{\text{Cu}(\text{NH}_3)_2^+/ \text{Cu}^0}^\circ - E_{\text{Cu}(\text{NH}_3)_4^{2+}/ \text{Cu}(\text{NH}_3)_2^+}^\circ &= 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_4^{2+}] \cdot [\text{NH}_3]^2}{[\text{Cu}(\text{NH}_3)_2^+][\text{NH}_3]^2[\text{Cu}(\text{NH}_3)_2^+]} \\
 &= 0.059 \log \frac{[\text{Cu}(\text{NH}_3)_4^{2+}]}{[\text{Cu}(\text{NH}_3)_2^+]^2} \\
 &= 0.059 \log K_{120}
 \end{aligned}$$

$$\begin{aligned}
 \therefore K_{120} &= 10^{[E_{\text{Cu}(\text{NH}_3)_2^+/ \text{Cu}^0}^\circ - E_{\text{Cu}(\text{NH}_3)_4^{2+}/ \text{Cu}(\text{NH}_3)_2^+}^\circ]/0.059} \\
 &= 10^{[-0.12 - (-0.01)]/0.059} \approx 10^{-2}
 \end{aligned}$$

Since K_{120} (10^{-2}) is much smaller than K_{120}° (1.73×10^6), the complexed $\text{Cu}(\text{NH}_3)_2^+$ ion is much less susceptible to disproportionation than the simple Cu^+ ion (i.e. $\text{Cu}(\text{aq})^+$ ion).

(iii) $\text{I}_2/2\text{I}^-$ Couples

Solubility of iodine (I_2) in water at ordinary temperature is very poor. A saturated solution of I_2 in water at 25°C is $\sim 1.33 \times 10^{-3} \text{M}$. Consequently, two types of half-reactions are possible for the $\text{I}_2/2\text{I}^-$ redox couple:



In a saturated solution of iodine in water, $\text{I}_2(\text{s})$ is in equilibrium with $\text{I}_2(\text{aq})$, so that the electrode potentials of the above two couples may be equated: $E_{(i)} = E_{(ii)}$.

$$E_{\text{I}_2(\text{aq})/2\text{I}^-}^\circ + \frac{0.059}{2} \log \frac{a_{\text{I}_2}}{a_{\text{I}^-}^2} = E_{\text{I}_2(\text{s})/2\text{I}^-}^\circ + \frac{0.059}{2} \log \frac{1}{a_{\text{I}^-}^2}$$

Activity of solid iodine $\text{I}_2(\text{s})$ is taken as unity.

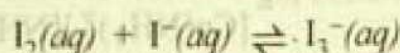
$$\begin{aligned}
 \therefore E_{\text{I}_2(\text{s})/2\text{I}^-}^\circ &= E_{\text{I}_2(\text{aq})/2\text{I}^-}^\circ + \frac{0.059}{2} \log a_{\text{I}_2} \\
 &\approx E_{\text{I}_2(\text{aq})/2\text{I}^-}^\circ + \frac{0.059}{2} \log C_{\text{I}_2} \quad (\text{for dilute solution})
 \end{aligned}$$

$$\therefore E_{I_2(s)/2I^-}^{\circ} = [0.6197 + 0.0295 \log (1.33 \times 10^{-3})]V$$

$$= 0.5348V$$

(where, C_{I_2} = analytical concentration of I_2 in water.)

Now, the enhancement of solubility of iodine in water in presence of soluble iodide (KI) due to the formation of triiodide (I_3^-) complex ion is well known;



$$K = \frac{[I_3^-]}{[I_2][I^-]} \approx 700 \text{ at } 25^\circ C.$$

$$\therefore [I_3^-] = K[I_2][I^-]$$

$$\therefore [I_2] = \frac{[I_3^-]}{K[I^-]}$$

It will be interesting to look into the change in the formal potential of $I_2/2I^-$ couple in presence of a specified concentration of iodide ion.

Substituting this equilibrium concentration of $[I_2]$ in the Nernst equation for the couple (i), we obtain,

$$\therefore E_{(i)} = E_{I_2(aq)/2I^-}^{\circ} + \frac{0.059}{2} \log_{10} \frac{[I_3^-]}{K[I^-]^3}$$

$$= \left(E_{I_2(aq)/2I^-}^{\circ} - 0.0295 \log K \right) + \frac{0.059}{2} \log_{10} \frac{[I_3^-]}{[I^-]^3}$$

$$\approx E_{I_3^-/3I^-}^f + \frac{0.059}{2} \log_{10} \frac{[I_3^-]}{[I^-]^3}$$

Thus, the new redox couple in presence of iodide ion is,



the formal potential of which is,

$$E_{I_3^-/3I^-}^f = E_{I_2(aq)/2I^-}^{\circ} - 0.0295 \log_{10} K$$

$$= 0.6197 - 0.0295 \log_{10} 700$$

$$= 0.5357V \approx 0.54V.$$

The electrode potential of this couple at specified concentration of iodide ion may be calculated as follows:

If C_{I^-} be the analytical concentration of I^- ion, then the mass balance equation of I^- ion will be,

$$C_{I^-} = [I^-] + [I_3^-] = [I^-](1 + K[I_2])$$

$$\therefore [I_3^-] = (C_{I^-} - [I^-]),$$

$$\therefore [I^-] = \frac{C_{I^-}}{1 + K[I_2]}$$

$$\therefore K = \frac{[I_3^-]}{[I^-][I_2]} = \frac{(C_{I^-} - [I^-])}{[I^-][I_2]} = 700$$

$$\text{and } [I_2] = 1.33 \times 10^{-3} \text{ M, (saturated solution at } 25^\circ\text{C)}$$

Therefore, when $C_{I^-} = 0.1 \text{ M}$

$$[I^-] = 0.0518 \text{ M and } [I_3^-] = 0.0482 \text{ M}$$

$$\therefore E_{(i)} = E_{I_3^-/3I^-}^{\circ} + \frac{0.059}{2} \log_{10} \frac{[I_3^-]}{[I^-]^3}$$

$$= \left[0.5357 + 0.0295 \log_{10} \frac{0.0482}{(0.0518)^3} \right] \text{ (V)}$$

$$= 0.611 \text{ V.}$$

The increase in the redox potential in this case is due to increase of in the concentration of the oxidized form of the couple, I_2 , from $[I_2] = 1.33 \times 10^{-3} \text{ M}$ to $[I_3^-] = 0.0482 \text{ M}$, in the form of the triiodide I_3^- complex ion due to its high stability constant. However, in presence of large excess of iodide (I^-) ion, the electrode potential of the couple slightly decreases as expected. Following the same procedure it may be shown that, if $C_{I^-} = 0.5 \text{ M}$ and $[I_2] = 1.33 \times 10^{-3} \text{ M}$ (i.e., saturated solution of I_2 in water at 25°C): $[I^-] = 0.259 \text{ M}$ and $[I_3^-] = 0.241 \text{ M}$,

$$\therefore E_{(i)} = \left[0.5357 + 0.0295 \log_{10} \frac{0.241}{(0.259)^3} \right] \text{ V} = 0.569 \text{ V.}$$

(j) Variation of Formal Potentials Due to Precipitation

Formation of sparingly soluble compounds by either or both the components of a redox couple greatly influences its redox property, since the effective concentration of a component in the solution is significantly lowered due to its precipitation. When a sparingly soluble salt or a compound is precipitated from a solution, the solution itself remains saturated with the

compound. If the precipitated substance is an electrolyte, its ions remain in equilibrium with its solid phase. That is, the *solubility product principle* comes into play and the effective concentrations of the redox active components are also influenced by the concentration of precipitating agent.

Consider a reversible redox couple consisting of two oxidation states of a metal, M^{n+} and $M^{(n-1)+}$ for the sake of simplicity,



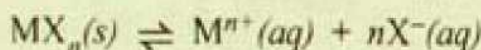
The Nernst equation for the redox potential (E) of this half-reaction in dilute solution will be,

$$E = E^\circ + 0.059 \log_{10} \frac{[M^{n+}]}{[M^{(n-1)+}]} \dots\dots (i)$$

where, E° is the standard redox potential of the half-reaction. In dilute solution, the activities of M^{n+} and $M^{(n-1)+}$ are almost equal to their equilibrium concentrations, []'s. If this redox couple occurs in the presence of a precipitating anion (X^-), which may form sparingly soluble salts MX_n and MX_{n-1} with M^{n+} and $M^{(n-1)+}$ ions respectively, three cases may arise depending upon the solubility products of MX_n and MX_{n-1} , concentration of the precipitating ion (X^-) and concentrations of the M^{n+} and $M^{(n-1)+}$ ions in the solution.

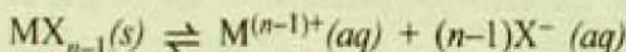
Case-1: Both MX_n and MX_{n-1} are sparingly soluble

The solubility equilibria of MX_n and MX_{n-1} may be expressed as,



$$(K_{sp})_n = [M^{n+}] [X^-]^n$$

$$\therefore [M^{n+}] = \frac{(K_{sp})_n}{[X^-]^n}$$



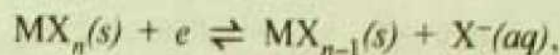
$$(K_{sp})_{n-1} = [M^{(n-1)+}] [X^-]^{n-1}$$

$$\therefore [M^{(n-1)+}] = \frac{(K_{sp})_{n-1}}{[X^-]^{n-1}}$$

Substituting these values $[M^{n+}]$ and $[M^{(n-1)+}]$ in the Nernst equation (i) for the $M^{n+}/M^{(n-1)+}$ couple one obtains,

$$\begin{aligned} E &= \left(E^\circ + 0.059 \log_{10} \frac{(K_{sp})_n}{(K_{sp})_{n-1} [X^-]} \right) (V) \\ &= (E^\circ + 0.059[p(K_{sp})_{n-1} - p(K_{sp})_n] + 0.059p[X]) \dots\dots (ii) \\ &= E^f \end{aligned}$$

where, E^f is the formal potential of the redox couple involving the two sparingly soluble salts: $MX_n(s)$ and $MX_{n-1}(s)$,



which is established in presence of the precipitating ion X^- . The magnitude of E^f is constant at a given concentration of X^- at a particular temperature. With increase of concentration of the precipitating agent X^- , the magnitude of E^f will decrease. At a given concentration of X^- ion, the magnitude of E^f will increase if $(K_{sp})_n > (K_{sp})_{n-1}$, that is, when the oxidized form MX_n is more soluble than the reduced form. On the other hand, if the oxidized form is less soluble than the reduced form, $(K_{sp})_n < (K_{sp})_{n-1}$, formal potential will decrease.

Example (2.44)

$$(1) \quad E^\circ(Fe^{3+}/Fe^{2+}) = +0.77V.$$

$$(K_{sp})_3 = K_{sp}[Fe(OH)_3] = 2.6 \times 10^{-39} \quad \therefore p(K_{sp})_3 \approx 38.6$$

$$(K_{sp})_2 = K_{sp}[Fe(OH)_2] = 4.9 \times 10^{-17} \quad \therefore p(K_{sp})_2 \approx 16.3$$

$$\therefore (K_{sp})_2 > (K_{sp})_3, \text{ i.e., } (pK_{sp})_3 > (pK_{sp})_2$$

$$\therefore E^f = E^\circ + 0.059 [p(K_{sp})_2 - p(K_{sp})_3] + 0.059 p[X]$$

$$\therefore E^f = \{+0.77V + [0.059(16.3 - 38.6) + 0.059 p[OH]]\}V$$

$$= (+0.77V - 1.32 + 0.059 p[OH])V$$

$$= (-0.55 + 0.059 p[OH])V$$

Thus, the formal potential is lower than E° , since $Fe(OH)_3$ is less soluble than $Fe(OH)_2$.

$$\therefore p[OH] = pK_w - p[H] = 14 - p[H] \text{ at } 25^\circ C.$$

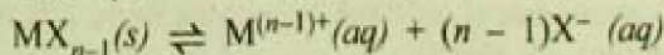
$$\therefore E^f = [-0.55 + 0.059(14 - p[H])] V$$

$$\approx (0.28 - 0.059 p[H])V.$$

Thus, it is seen that with increase of OH^- ion concentration, i.e., with increase of $p[H]$, the formal potential of Fe^{3+}/Fe^{2+} couple will decrease (cf. Fig. 2.7)

Case - 2: When the oxidized form MX_n is soluble but the reduced form MX_{n-1} is sparingly soluble

The solubility equilibrium of only MX_{n-1} is to be considered,



$$(K_{sp})_{n-1} = [M^{(n-1)+}][X^-]^{(n-1)}$$

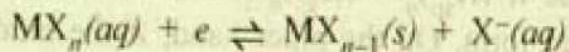
$$\therefore [M^{(n+1)+}] = \frac{(K_{sp})_{n-1}}{[X^-]^{n-1}}$$

Substituting for $[M^{(n-1)+}]$ in the Nernst equation (i) of the $M^{n+} / M^{(n-1)+}$ redox couple, one obtains,

$$\begin{aligned}
 E &= E^\circ + 0.059 \log_{10} \frac{[M^{n+}][X^-]^{n-1}}{(K_{sp})_{n-1}} \\
 &= E^\circ + 0.059 p(K_{sp})_{n-1} + 0.059 (n-1) \log_{10} [X^-] + 0.059 \log_{10} [M^{n+}] \\
 &= E^f + 0.059 \log_{10} [M^{n+}]
 \end{aligned}$$

where, $E^f = E^\circ + 0.059 p(K_{sp})_{n-1} + 0.059 (n-1) \log_{10} [X^-]$,

which is the formal potential of the redox couple,



The magnitude of E^f at a given concentration of the precipitant X^- ion, at a particular temperature will depend upon the solubility product $(K_{sp})_{n-1}$ of MX_{n-1} . If $(K_{sp})_{n-1}$ is very small, $p(K_{sp})_{n-1}$ is large, E^f is also large, since the concentration of the reduced component is less.

Examples (2.45)

(1) $Cu^{2+}/CuI(s)$ system

$$E^\circ (Cu^{2+}/Cu^+) = +0.15V$$

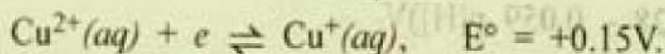
$$E^\circ (I_2/2I^-) = +0.53V$$

$$K_{sp} [CuI] = 11 \times 10^{-12}$$

$$\therefore pK_{sp} = 11.96$$

Since $E^\circ (Cu^{2+}/Cu^+) < E^\circ (I_2/2I^-)$, Cu^{2+} ion should not oxidize I^- to liberate I_2 . But it does so, as because, due to low solubility, CuI precipitates, leaving Cu^{2+} ions in solution. As a result, formal potential of the (Cu^{2+}/Cu^+) couple increases to $\sim 0.8V$ and eventually Cu^{2+} quantitatively oxidizes iodide to liberate iodine. This reaction forms the basis of iodometric estimation of copper.

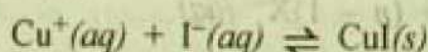
The half-reaction of the Cu^{2+}/Cu^+ couple is,



The Nernst equation for this couple in dilute solution may be written as,

$$E = E^\circ + 0.059 \log_{10} \frac{[Cu^{2+}]}{[Cu^+]}$$

In presence of iodide ion, Cu^+ is removed from the equilibrium due to precipitation of sparingly soluble $CuI(s)$,



$$K_{sp} = [Cu^+][I^-]$$

$$\therefore [Cu^+] = \frac{K_{sp}}{[I^-]}$$

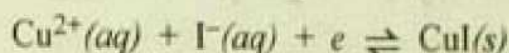
Substituting this value of $[Cu^+]$ in the Nernst equation of Cu^{2+}/Cu^+ couple, one obtains,

$$E = E^\circ + 0.059pK_{sp} + 0.059 \log_{10}[I^-] + 0.059 \log_{10}[Cu^{2+}]$$

$$= E^f + 0.059 \log_{10}[Cu^{2+}]$$

where, $E^f = E^\circ + 0.059pK_{sp} + 0.059 \log_{10}[I^-]$,

which corresponds to the formal potential of the half-reaction,



The magnitude of E^f depends upon the concentration of I^- ion in the solution. If to a dilute solution of Cu^{2+} an excess of iodide ion is added, the total concentration of iodide ion, C_{I^-} may be taken as the equilibrium concentration $[I^-]$ of iodide. Suppose $C_{I^-} = 0.1(M)$, (i.e., $\sim 1.66g$ of KI per 100 ml) then the value of E^f will be,

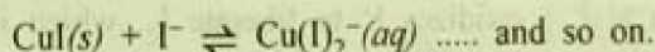
$$E^f = (+0.15 + 0.059 \times 11.96 + 0.059 \log_{10}[0.1]) V \approx 0.797V = 0.8V$$

Since the formal potential of this Cu^{2+} , $I^-/CuI(s)$ couple much exceeds the standard potential of $I_2/2I^-$ couple, in presence of sufficient excess of I^- ion, Cu^{2+} ion oxidizes iodide ion to liberate iodine with precipitation of $CuI(s)$. The net reaction is,



Thus, if an inorganic mixture contains a copper salt and an iodide salt, the sample on dissolution or even in the solid state in presence of little moisture, gradually turns dark brown coloured due to adsorption of the liberated iodine by the solid materials, particularly the $CuI(s)$, that is formed due to reduction of Cu^{2+} by I^- ion.

Note: In presence of large excess of soluble iodide, the precipitate of CuI passes into solution due to complex formation:

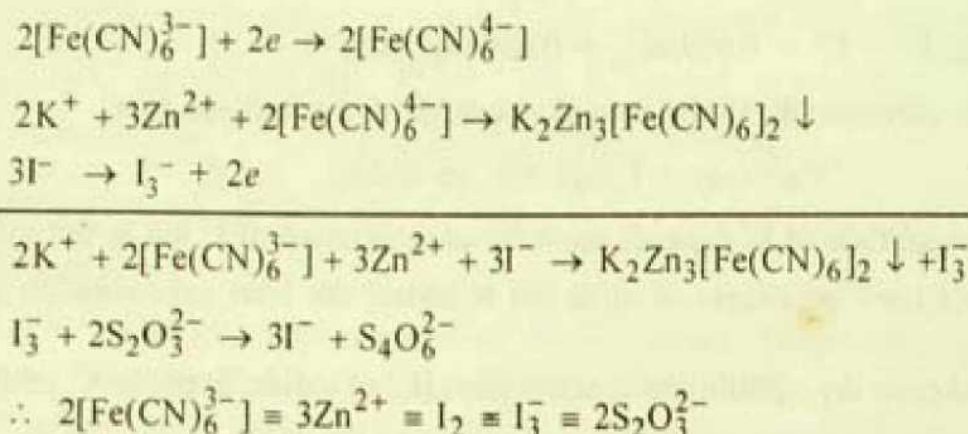


(2) The ferricyanide-ferrocyanide half-reaction



Formal potential of this couple at $pH \sim 3$ is $\sim +0.46V$ due to relatively higher degree of protonation of $[Fe(CN)_6]^{4-}$ ion relative to $[Fe(CN)_6]^{3-}$ ion (cf. Sect 2.4.(h)). As such, ferricyanide ion can not oxidize iodide ion to liberate iodine under this condition, since, $E_{I_2/2I^-}^\circ = 0.53V$. But if a small amount of Zn^{2+} ion is also present in a ferricyanide-ferrocyanide mixture, ferrocyanide is precipitated as sparingly soluble potassium zinc ferrocyanide, $K_2Zn_3[Fe(CN)_6]_2$, leaving ferricyanide ion in solution. Although zinc ferricyanide is also sparingly soluble, but $K_2Zn_3[Fe(CN)_6]_2$ is much less soluble than zinc ferricyanide. Due to removal of the reductant component, i.e., $[Fe(CN)_6]^{4-}$ ion, from the redox equilibrium, formal potential of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple increases significantly. As a result of that,

ferricyanide ion can quantitatively oxidize iodide to liberate iodine, which can be estimated by titration with standard sodium thiosulfate solution.

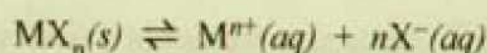


This reaction forms the basis of iodometric estimation of Zn^{2+} and also of ferricyanide.

In qualitative inorganic analysis if a solution contains both iodide and Zn^{2+} ions, a dark brown colouration or precipitate appears on addition of a drop of ferricyanide solution, due to oxidation of iodide to iodine by ferricyanide and adsorption of liberated I_2 by the precipitated salt, $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. If a solution contains ferricyanide, ferrocyanide and iodide, it will be orange coloured at neutral pH due to ferricyanide. On acidification ($\text{pH} \leq 1$), the colour of the solution turns brown due to iodine, as iodide is oxidized by ferricyanide in acid medium (cf. Sect 2.4.(h)). On the other hand, if a soluble zinc-salt is added to a neutral solution containing $[\text{Fe}(\text{CN})_6^{3-}]$, $[\text{Fe}(\text{CN})_6^{4-}]$ and I^- , a brown colouration or a precipitate appears as zincferrocyanide (more appropriately, $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$) is precipitated, leaving ferricyanide ions in solution. As a result, formal potential of $[\text{Fe}(\text{CN})_6^{3-}] / [\text{Fe}(\text{CN})_6^{4-}]$ couple exceeds the E° of $\text{I}_2/2\text{I}^-$ couple and $[\text{Fe}(\text{CN})_6^{3-}]$ oxidizes I^- to liberate I_2 , which is adsorbed by the precipitate of $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$. However, the brown colour of I_2 may be discharged by adding drops of sodium thiosulfate solution or SO_2 -water or it may be extracted out by shaking with CCl_4 or CHCl_3 . Tests for other cation and anion radicals may be performed after decomposing / removing the excess reagent from the test solution accordingly.

Case - 3. MX_n is sparingly soluble MX_{n-1} is soluble

The solubility equilibrium of only MX_n is involved along with the redox equilibrium,



$$(\text{K}_{sp})_n = [\text{M}^{n+}][\text{X}^-]^n$$

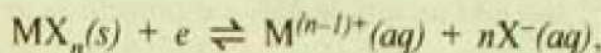
$$\therefore [\text{M}^{n+}] = \frac{(\text{K}_{sp})_n}{[\text{X}^-]^n}$$

Substituting this value of $[\text{M}^{n+}]$ in the Nernst equation (i) of the $\text{M}^{n+}/\text{M}^{(n-1)+}$ couple, one obtains,

$$\begin{aligned}
 E &= E^\circ + 0.059 \log_{10} \frac{(K_{sp})_n}{[M^{(n-1)+}][X^-]^n} \\
 &= (E^\circ - 0.059 p(K_{sp})_n - 0.059 n \log_{10}[X^-] - 0.059 \log_{10}[M^{(n-1)+}]) \\
 &= E^f - 0.059 \log_{10}[M^{(n-1)+}]
 \end{aligned}$$

where, $E^f = E^\circ - 0.059 p(K_{sp})_n - 0.059 n \log_{10}[X^-]$

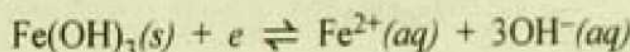
which is the formal potential of the redox couple,



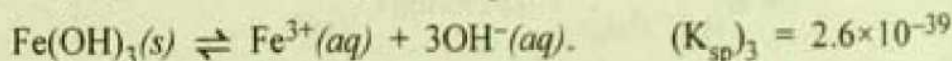
that exists in presence of the precipitating agent X^- . E^f at a particular temperature is a function of the concentration of the precipitating agent X^- . As the concentration of X^- increases, E^f decreases. At a given concentration of X^- , E^f increases as $(K_{sp})_n$ increases (i.e., as $p(K_{sp})_n$ decreases), and vice-versa. Therefore, the less soluble is MX_n , the lower is the formal potential at a given concentration of X^- ion.

Examples (2.46)

(1) τ most common example is again the Fe^{3+}/Fe^{2+} system. Consider the part of the Pourbaix diagram (cf. Sect. 2.4.1(iii)) of iron (Fig. 2.7) in the region between pH 4 to pH 8-9, where $Fe(OH)_3(s)$ is in redox equilibrium with $Fe^{2+}(aq)$ ion according to the half-reaction,



Thus, the solubility equilibrium of only $Fe(OH)_3(s)$ is involved with the redox equilibrium,



$$(K_{sp})_3 = [Fe^{3+}][OH^-]^3 = 2.6 \times 10^{-39} \quad \therefore p(K_{sp})_3 = 38.6$$

$$\therefore [Fe^{3+}] = \frac{(K_{sp})_3}{[OH^-]^3} = \frac{(K_{sp})_3}{(K_w/[H^+])^3} = \frac{(K_{sp})_3[H^+]^3}{(K_w)^3}$$

$$\therefore K_w = [H^+][OH^-] = 10^{-14} \text{ (at } 25^\circ\text{C)}$$

Substituting the above value of $[Fe^{3+}]$ in the Nernst equation for the Fe^{3+}/Fe^{2+} couple we obtain,

$$\begin{aligned}
 E &= E^\circ + 0.059 \log_{10} \left[\frac{(K_{sp})_3[H^+]^3}{(K_w)^3[Fe^{2+}]} \right] \\
 &= E^\circ + 0.059 \log_{10}(K_{sp})_3 - 0.059 \times 3 \log K_w + 0.059 \times 3 \log_{10}[H^+] - 0.059 \log_{10}[Fe^{2+}] \\
 &= (E^\circ - 0.059 p(K_{sp})_3 + 0.177 pK_w - 0.177 p[H]) - 0.059 \log_{10}[Fe^{2+}] \\
 &= (E^f - 0.059 \log_{10}[Fe^{2+}]) \text{ V.}
 \end{aligned}$$

where, $E^f = (E^\circ - 0.059 p(K_{sp})_3 + 0.177 pK_w - 0.177 p[H]) \text{ V.}$

which is the formal potential of the $\text{Fe}(\text{OH})_3(s)/\text{Fe}^{2+}(aq)$ couple. At a particular temperature, as the $p[\text{H}]$ increases (i.e. the concentration of OH^- increases) the formal E^f decreases, as more and more of the oxidant component is precipitated. At a particular $p[\text{H}]$, the less soluble is the oxidized form, i.e. less is (K_{sp}) , (here $(K_{sp})_3$) the lower is the formal potential. Formal potential of the $\text{Fe}(\text{OH})_3(s)/\text{Fe}^{2+}(aq)$ couple at $p[\text{H}]$ 7 will be:

$$E^f = (+0.77 - 0.059 \times 38.6 + 0.177 \times 14 - 0.177 \times 7) \text{ V} = -0.27\text{V}.$$

Fe^{III} shows its oxidizing property mainly in acidic solution, whereas, Fe^{II} becomes strongly reducing in basic medium. If a Fe^{III} salt and an iodide salt are present is an inorganic mixture, Fe^{3+} will oxidize I^- to liberate I_2 in acidic solution [$\because E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = 0.77\text{V}$, $E^\circ(\text{I}_2/2\text{I}^-) = +0.53\text{V}$]. But in the Na_2CO_3 extract, iodide will remain as such, since Na_2CO_3 extract is strongly alkaline and Fe^{3+} will precipitate as $\text{Fe}(\text{OH})_3$. As a result, formal potential of $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ couple will be even lower than that of the $\text{I}_2/2\text{I}^-$ couple.

(2) $\text{Hg}_2^{2+}/2\text{Hg}^\circ(l)$ couple in presence of chloride ion

The Nernst equation for the half- reaction,



may be written as,

$$E = E^\circ_{\text{Hg}_2^{2+}/2\text{Hg}^\circ} + \frac{0.059}{2} \log[\text{Hg}_2^{2+}]$$

$$\approx E^f_{\text{Hg}_2^{2+}/2\text{Hg}^\circ} + 0.0295 \log C_{\text{Hg}_2^{2+}}$$

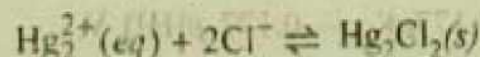
where, $E^f_{\text{Hg}_2^{2+}/2\text{Hg}^\circ}$ is the formal potential of this redox couple. Since the formal potential,

$E^f_{\text{Hg}_2^{2+}/2\text{Hg}^\circ}$ is 0.776V in 1M HClO_4 , the electrode potential(E) of the system with

$C_{\text{Hg}_2^{2+}} = 0.01\text{M}$ under this condition will be,

$$E = [0.776 + \frac{0.059}{2} \log_{10}(0.01)] \text{ V} = 0.717 \text{ V}$$

Thus, the $\text{Hg}_2^{2+} / 2\text{Hg}^\circ$ couple appears to be a moderately oxidizing couple. Such a couple may be transformed into a reducing couple, either by keeping the $C_{\text{Hg}_2^{2+}}$ very low, or, by removing Hg_2^{2+} ion from the solution by complex formation, or, precipitation. It is well known that on addition of chloride ion to mercurous ion solution, mercurous chloride (*calomel*, Hg_2Cl_2 , $K_{sp} = 1.32 \times 10^{-18}$ at 25°C) is precipitated:



$$K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2 = 1.32 \times 10^{-18} \text{ (at } 25^\circ\text{C)}$$

$$\therefore [\text{Hg}_2^{2+}] = \frac{K_{sp}}{[\text{Cl}^-]^2}$$

Substituting this value of $[\text{Hg}_2^{2+}]$ in the Nernst equation of $\text{Hg}_2^{2+}/2\text{Hg}^\circ$ couple, and assuming dilute solution, (i.e., $E^\circ \approx E^\circ$) one obtains:

$$\begin{aligned} E &= E^\circ_{\text{Hg}_2^{2+}/2\text{Hg}^\circ} + \frac{0.059}{2} \log_{10} \frac{K_{sp}}{[\text{Cl}^-]^2} \\ &= \left(E^\circ_{\text{Hg}_2^{2+}/2\text{Hg}^\circ} + 0.0295 \log K_{sp} \right) - 0.059 \log_{10} [\text{Cl}^-] \\ &= E^f_{\text{Hg}_2^{2+}/2\text{Hg}^\circ} - 0.059 \log [\text{Cl}^-] \end{aligned}$$

Thus, the electrode potential of $\text{Hg}_2^{2+}/2\text{Hg}^\circ(l)$ couple depends upon Cl^- ion concentration. With increase of Cl^- ion concentration (E) decreases and the system becomes more and more reducing. The above equation is the Nernst equation for the half-reaction,



as occurs in *calomel electrode*. The formal potential of the electrode is given by,

$$\begin{aligned} E^f_{\text{Hg}_2^{2+}/2\text{Hg}^\circ} &= E^\circ_{\text{Hg}_2^{2+}/2\text{Hg}^\circ} + 0.0295 \log K_{sp} \\ &= 0.80\text{V} + 0.0295 \times \log(1.32 \times 10^{-18}) \\ &= 0.273\text{V} \end{aligned}$$

Thus, in presence of chloride ion, the oxidizing power of the $\text{Hg}_2^{2+}/2\text{Hg}^\circ$ couple is significantly reduced due to precipitation of the oxidant component (Hg_2^{2+}) of the couple in the form of $\text{Hg}_2\text{Cl}_2(s)$. This is evident from the decrease of formal potentials of three types of *calomel electrodes* with increase of Cl^- ion concentration.

For chloride ion concentration of 0.1M (*decimolar*), 1M (*molar*) and 4.75M (approximately saturated) KCl at 25°C the potential (E) of the $\text{Hg}_2^{2+}/2\text{Hg}^\circ$ electrode, according to the equation,

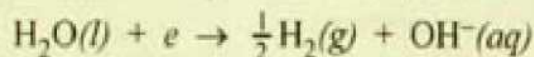
$$\begin{aligned} E &= \left(E^f_{\text{Hg}_2^{2+}/2\text{Hg}^\circ} - 0.059 \log [\text{Cl}^-] \right) \text{V} \\ &= (0.273 - 0.059 \log [\text{Cl}^-])\text{V} \end{aligned}$$

will be 0.332V , 0.273V and 0.233V respectively at 25°C . Literature values of the potentials

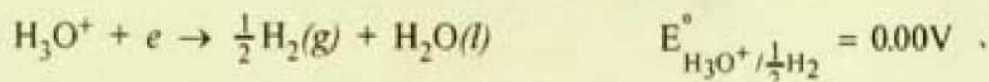
of decinormal, normal and saturated (KCl, SCE) calomel electrodes at 25°C are 0.3358V, 0.2824V and 0.2444V respectively vs. standard hydrogen electrode (SHE).

(k). Redox Stability Field of Water

Water can act both as an oxidizing agent as well as a reducing agent. When water acts as an oxidizing agent, it is reduced to hydrogen gas according to the half-reaction,



which in fact is similar to the reduction of hydronium ion,



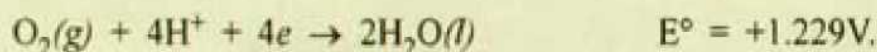
The Nernst equation for the electrode potential for these half-reactions is,

$$E_{\text{H}_3\text{O}^+/\frac{1}{2}\text{H}_2} = E^\circ_{\text{H}_3\text{O}^+/\frac{1}{2}\text{H}_2} + 0.059 \log_{10} \frac{a_{\text{H}_3\text{O}^+}}{(\text{pH}_2)^{1/2}}$$

If the partial pressure of hydrogen gas (pH_2) is equal to 1 atm, the electrode potential of the above half-cell will be,

$$E_{\text{H}_3\text{O}^+/\frac{1}{2}\text{H}_2} = 0 + 0.059 \log_{10} a_{\text{H}_3\text{O}^+} = -(0.059 \text{pH})\text{V} \quad \dots (i)$$

When water acts as a reducing agent, it is oxidized to oxygen gas according to the half-reaction,



The Nernst equation for this half-cell is

$$E_{\text{O}_2/2\text{H}_2\text{O}} = E^\circ_{\text{O}_2/2\text{H}_2\text{O}} + \frac{0.059}{4} \log_{10} (a_{\text{H}^+})^4 (\text{pO}_2)$$

If the partial pressure (pO_2) of oxygen gas is equal to 1 atm, the potential of the above half-cell becomes,

$$E_{\text{O}_2/2\text{H}_2\text{O}} = \left(1.229 + \frac{0.059}{4} \times 4 \log_{10} a_{\text{H}^+} \right) \text{V} = (1.229 - 0.059 \text{pH})\text{V} \quad \dots (ii)$$

Thus, the two equations (i) and (ii) represent the variation of redox potentials of the $\text{H}_2\text{O}(l)/\frac{1}{2}\text{H}_2(g)$ and $\text{O}_2(g)/2\text{H}_2\text{O}(l)$ redox couples representing respectively the reduction and oxidation of water. If the potential is plotted against pH, both the equations will produce straight lines of slope - 0.059, that is, the two straight lines will be parallel and will be inclined from higher (positive) value of potential to lower positive or higher negative values with increase of pH (Fig. 2.3). The straight line representing reduction of water (equation (i)) does not make any intercept on the potential axis. It starts from zero of potentials (i.e. $E = 0.0\text{V}$ at $\text{pH} = 0$, i.e. 1M acid). The straight line representing oxidation of water (equation (ii)) makes an intercept of +1.229V on the potential axis ($E = +1.229\text{V}$ at $\text{pH} = 0$ i.e. 1M acid). At the two extremes

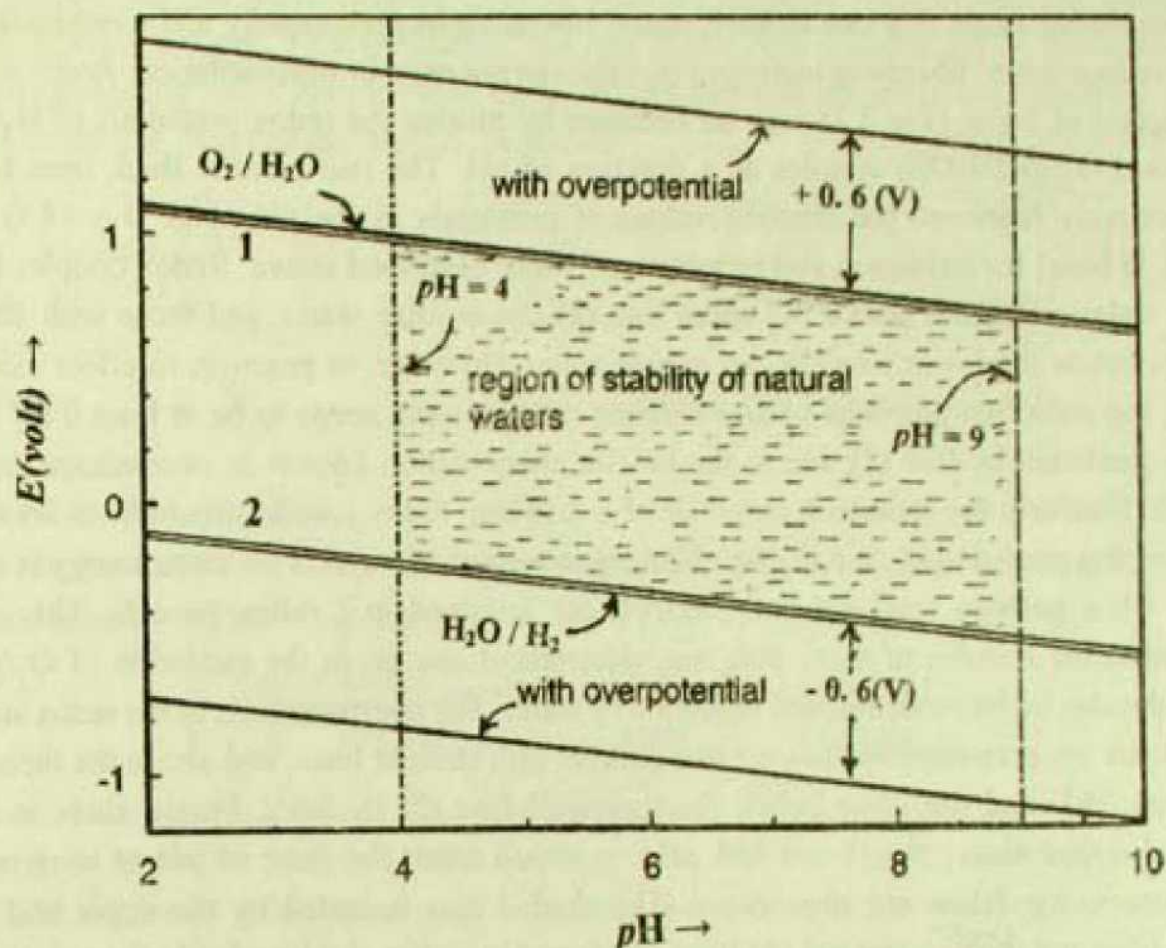


Fig. 2.3. Redox stability field of water.

of the pH limit of water, i.e., $pH = 0$ (1 M acid) to $pH = 14$ (1 M base, since $pK_w = 14$) and at neutral $pH = 7$, the potentials of the above two half-cell reactions are given below:

	$pH = 0$ (1 M acid)	$pH = 7$ (neutral)	$pH = 14$ (1 M base)
$E_{O_2/2H_2O}$ (V)	+1.229	+0.815	+0.404
$E_{H_3O^+/\frac{1}{2}H_2}$ (V)	0	-0.414	-0.828

The half-cell reactions for reduction and oxidation of water in 1 M acid ($pH = 0$), neutral medium ($pH = 7$) and in 1 M base ($pH = 14$) are summarized below:

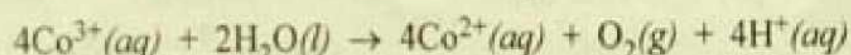
Conditions	Half-cell reactions	E° (V)
<i>Reduction of water</i>		
1 M acid ($pH = 0$)	$H_3O^+(aq) + e \rightarrow \frac{1}{2}H_2(g) + H_2O(l)$	0.00
Neutral medium ($pH = 7$)	$H_2O(l) + e \rightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	-0.414
1 M base ($pH = 14$)	$H_2O(l) + e \rightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	-0.828
<i>Oxidation of water</i>		
1 M acid ($pH = 0$)	$H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e$	-1.229
Neutral medium ($pH = 7$)	$H_2O(l) \rightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e$	-0.815
1 M base ($pH = 14$)	$2OH^-(aq) \rightarrow \frac{1}{2}O_2(g) + H_2O + 2e$	-0.401

An oxidizing agent that can oxidize water, liberating oxygen rapidly and a reducing agent that can reduce water, liberating hydrogen rapidly, can not exist in water solution. *Redox stability field* diagram of water (Fig 2.3) may be obtained by plotting the redox potentials of $\text{H}_3\text{O}^+ (l)/\frac{1}{2}\text{H}_2(g)$ and $\text{O}_2(g)/2\text{H}_2\text{O}(l)$ couples as a function of $p\text{H}$. The two parallel thick lines (1) and (2) respectively represent the limiting values of potentials in the $p\text{H}$ range 0 – 14 (i.e. 1M acid to 1 M base) for oxidation and reduction of water described above. Redox couples having standard redox potentials above the upper line (1) can oxidize water, and those with standard potentials below the lower line (2) can reduce water. However, in practice, to effect oxidation of water, the reduction potential of an oxidizing redox couple needs to be at least 0.6V higher than that predicted by line (1) due to the kinetic phenomenon known as *overvoltage* (or *over potential*). Similarly the reduction potential of a reducing redox couple should be at least 0.6V lower than that predicted by line (2) for effecting reduction of water. This extra energy is always required when gaseous reactants and products are involved in a redox process. This is also associated to the transfer of more than one electrons at one go in the evolution of $\text{O}_2(g)$ and $\text{H}_2(g)$ molecules in the oxidation and reduction of water. The overpotentials in the redox stability field of water are presented by drawing two parallel thin straight lines, one above the theoretical line (1) by 0.6V and the other below the theoretical line (2) by 0.6V. Finally, there is a pair of vertical dotted lines at $p\text{H} = 4$ and $p\text{H} = 9$, which mark the limit of $p\text{H}$ of most natural water sources, e.g. lakes and streams etc. The shaded area bounded by the upper and lower potential lines and the two vertical $p\text{H}$ lines is referred to as the *stability field of natural waters*.

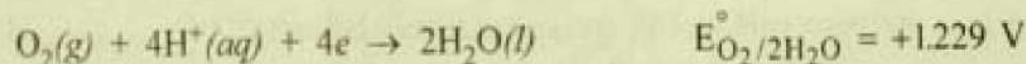
Examples (2.47)

(1) Oxidation of water

(i) $\text{Co}^{3+}(aq)$ oxidizes water with evolution of $\text{O}_2(g)$ according to,



The two redox couples involved in this reaction are,



If a cell is constructed by coupling these two half-cells, the *emf* of the cell will be,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = E_{\text{Co}^{3+}/\text{Co}^{2+}}^\circ - E_{\text{O}_2/2\text{H}_2\text{O}}^\circ = (1.92 - 1.229)\text{V} \approx +0.69\text{V}$$

As the cell *emf* is close to the overpotential for O_2 evolution, the reaction will proceed in the right direction. Since H^+ ions are produced, the reaction, will be favoured on removal of H^+ ions i.e. by increasing the $p\text{H}$, which lowers the redox potential of the $\text{O}_2/2\text{H}_2\text{O}$ couple, whereas, that of the $\text{Co}^{3+}/\text{Co}^{2+}$ couple remains unchanged.

(ii) Reduction potentials of $\text{Ce}^{4+}/\text{Ce}^{3+}$ ($E^\circ = +1.76\text{V}$) and acidified solutions of $\text{MnO}_4^-/\text{H}^+/\text{Mn}^{2+}$ ($E^\circ = +1.51\text{V}$); $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+/2\text{Cr}^{3+}$ ($E^\circ = +1.33\text{V}$) are higher than that of the $\text{O}_2/$

$2\text{H}_2\text{O}$ couple, but yet these couples exist in aqueous solution without causing oxidation of water to liberate oxygen. This is because, the *emf* of the cells constructed by combining these otherwise oxidizing redox couples with the $\text{O}_2/2\text{H}_2\text{O}$ half-cell are all lower than 0.6V required to overcome the overvoltage for O_2 evolution:

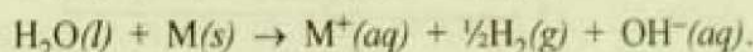
$$E^\circ_{(\text{Ce}^{4+}/\text{Ce}^{3+})} - E^\circ_{(\text{O}_2/2\text{H}_2\text{O})} = (1.76 - 1.229)\text{V} \approx 0.53\text{V}$$

$$E^\circ_{(\text{MnO}_4^-, \text{H}^+/\text{Mn}^{2+})} - E^\circ_{(\text{O}_2/2\text{H}_2\text{O})} = (1.51 - 1.229)\text{V} \approx 0.28\text{V}$$

$$E^\circ_{(\text{Cr}_2\text{O}_7^{2-}, \text{H}^+/\text{Cr}^{3+})} - E^\circ_{(\text{O}_2/2\text{H}_2\text{O})} = (1.33 - 1.229)\text{V} \approx 0.1\text{V}$$

(2) Reduction of water

(1) Most *s*-block metals react with water or aqueous acid solutions evolving H_2 gas. The reactions actually involve reduction of H^+ ions or H_2O molecules:



where, M is a *s*-block alkali metal. Similar reactions may occur with certain *s*-block alkaline earth and 3d transition metals (Ti, V, Cr, Mn). The difference in the standard potentials of the M^{n+}/M and the $\text{H}^+/\frac{1}{2}\text{H}_2$ redox couples in 1 M acid medium are greater than the overpotential required for H_2 evolution:

$$\left(E^\circ_{\text{M}^{n+}/\text{M}} - E^\circ_{\text{H}^+/\frac{1}{2}\text{H}_2} \right) = \left(E^\circ_{\text{M}^{n+}/\text{M}} - 0 \right) = E^\circ_{\text{M}^{n+}/\text{M}}$$

M	Li	Na	K	Mg	Al	Ca	Ti	Cr	Mn
$E^\circ_{\text{M}^{n+}/\text{M}} (\text{V})$	-3.04	-2.713	-2.924	-2.36	-1.68	-2.87	-1.63	-0.90	-1.18

Although the redox potential difference of Mg^{2+}/Mg and Al^{3+}/Al couples with that of the $\text{H}^+/\frac{1}{2}\text{H}_2$ couple exceeds the overpotential barrier of -0.6V, yet these metals may be used to handle water in presence of air for long period. This is because the metals react spontaneously on exposure to moist air, when an impervious thin film of oxide is formed on the metal surface, which is rendered passive and protected against attack by water. Fe, Cr, Zn are similarly passivated.

(I) Redox potential diagrams

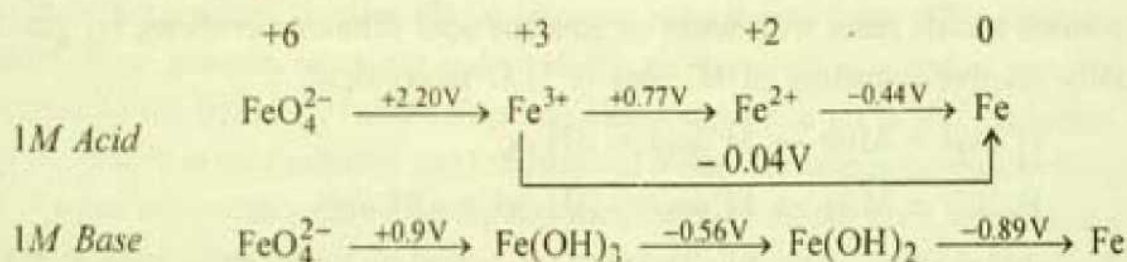
Redox potential diagrams are extremely useful in predicting the ability of different oxidation states of an element to undergo oxidation, reduction, disproportionation and comproportionation reactions. Three types of redox potential diagrams are useful in inorganic analysis.

(i) Latimer diagrams

Latimer diagrams (or, reduction potential diagrams) present the standard potentials connecting the various oxidation states of a particular element. In these diagrams the standard

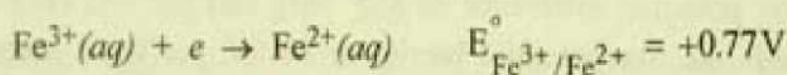
reduction potentials for the reduction half-cell reactions involving two oxidation states of an element are joined by a left to right arrow ($\rightarrow$) from the higher oxidation state at the left to the lower oxidation state of the redox couple to the right. Various oxidation states of the element are shown by integer numbers above or below the respective species with (+) and (-) signs as required. Latimer diagrams of an element may be constructed with the standard reduction potential values corresponding to the species existing in 1 M acid, in neutral ($pH = 7$) as well as to the species existing in 1 M base solutions for various oxidation states of an element, putting the highest oxidation state on the left hand side and the lowest oxidation state on the right hand side. Redox potential in volt (V) of the couples involving two oxidation states are stated above the line joining these two oxidation states.

The Latimer diagrams of iron in acidic and basic solutions are shown below:



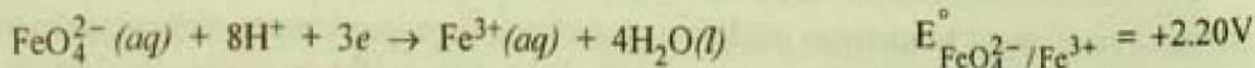
From the Latimer diagram of an element it is possible to predict the redox behaviour of a given species of the element. The more positive is the value of standard reduction potential the more readily the species on the L.H.S. is reduced to the species on the R.H.S. of the arrow. Strong oxidizing agents are characterised with high positive values of the standard reduction potentials and occur to the left of the diagram. Strong reducing agents are characterized by high negative values of the standard potentials and occur to the right of the diagram.

It is possible to write the half-reaction of a redox couple from their positions on the Latimer diagram. As for example the half-reaction for reduction of Fe^{3+} to Fe^{2+} in 1 M acid may be written as.

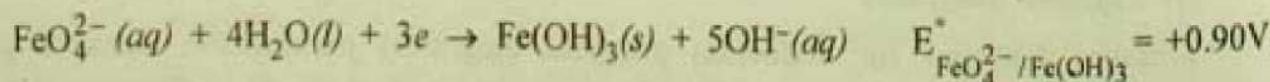


Half-reactions for reduction of oxo ions should be written in such a manner that the O-atoms are balanced by transformation into H_2O molecules, H-atoms in the resulting H_2O molecules tally with the H^+ ions, and finally balancing the charge with electrons. For the ferrate, FeO_4^{2-} ion, we can write,

In 1M acid medium



In 1M basic medium





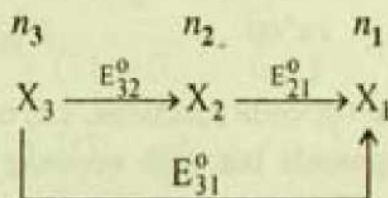
Thus, the oxo anion, FeO_4^{2-} is a stronger oxidant in acid medium [$E^\circ(\text{FeO}_4^{2-}/\text{Fe}^{3+}) = +2.20\text{V}$] than in basic medium [$E^\circ(\text{FeO}_4^{2-}/\text{Fe}(\text{OH})_3) = +0.90\text{V}$].

On the other hand, in acid solution Fe^{2+} is quite stable toward oxidation to Fe^{3+} (-0.77V), but in basic solution $\text{Fe}(\text{OH})_2$ is readily oxidized to $\text{Fe}(\text{OH})_3$ ($+0.56\text{V}$).

Although Latimer diagrams are very useful in identifying the actual redox species of an element, nevertheless these diagrams for elements existing in several oxidation states and involving protons, hydroxo and oxo species are very complex and sorting out information from such diagrams are tedious.

Since Latimer diagram of an element portrays the standard potentials of the redox couples of the element diagrammatically, where oxidation numbers decrease from left to right and the $E^\circ(\text{V})$ values are written above the right handed arrows joining the two components of the redox couples, these diagrams are very useful in predicting the possible redox reactions the atoms and the ions of an element can undergo.

Standard potentials (E°) of redox couples involving the adjacent oxidation numbers are given on the Latimer diagram. E° values of some couples involving non-adjacent oxidation numbers are also given in case of some elements. The E° values of couples involving non-adjacent oxidation numbers may be calculated from the E° values of the intermediate adjacent couples with the aid of the relation, $\Delta G^\circ = -nFE^\circ$ and taking the overall free energy change as the sum of the free energy changes of the intermediate steps. Consider the Latimer diagram of the element X, in which the element exists in n_1 , n_2 and n_3 oxidation states ($n_3 > n_2 > n_1$) and the corresponding species of X are X_1 , X_2 and X_3 respectively.



E_{21}° and E_{32}° are the standard potentials of the two adjacent couples X_2/X_1 and X_3/X_2 .

The standard potential E_{31}° of the non-adjacent X_3/X_1 couple maybe related to E_{21}° and E_{32}° .

If ΔG_{21}° , ΔG_{32}° and ΔG_{31}° be the standard free energy changes associated with the electrode reactions of the corresponding couples, then,

$$\Delta G_{21}^\circ = -(n_2 - n_1)F E_{21}^\circ$$

$$\Delta G_{32}^\circ = -(n_3 - n_2)F E_{32}^\circ$$

$$\Delta G_{31}^\circ = -(n_3 - n_1)F E_{31}^\circ$$

$$\therefore \Delta G_{31}^\circ = \Delta G_{32}^\circ + \Delta G_{21}^\circ$$

$$\therefore -(n_3 - n_1)F E_{31}^{\circ} = [-(n_3 - n_2)F E_{32}^{\circ}] + [-(n_2 - n_1)F E_{21}^{\circ}]$$

$$\therefore (n_3 - n_1)E_{31}^{\circ} = (n_3 - n_2)E_{32}^{\circ} + (n_2 - n_1)E_{21}^{\circ}$$

$$\therefore E_{31}^{\circ} = \frac{(n_3 - n_2)E_{32}^{\circ} + (n_2 - n_1)E_{21}^{\circ}}{(n_3 - n_1)}$$

Another method of calculation of standard redox potential of an intermediate couple (i.e. of the type X_3/X_2) has been discussed earlier (cf. p. 125)

Consider the Latimer diagram of iron in 1 M acid medium presented earlier. The E° values of Fe^{3+}/Fe^{2+} and Fe^{2+}/Fe° couples are $E_{32}^{\circ} = +0.77V$ and $E_{20}^{\circ} = -0.44V$ respectively. The E° value of the Fe^{3+}/Fe° couple (i.e. E_{30}°) may be calculated using the above relation, where, $n_3 = +3$, $n_2 = +2$, $n_1 = 0$.

$$\begin{aligned} E^{\circ}(Fe^{3+} / Fe^{\circ}) = E_{30}^{\circ} &= \frac{[(+3) - (+2)] \times (0.77) + [(+2) - (0)] \times (-0.44)}{(+3 - 0)} V \\ &= \frac{0.77 + 2 \times (-0.44)}{3} = -0.0367V \approx -0.04V \end{aligned}$$

Since the E° values for the reduction half-cell reactions are negative,



therefore, the E° values for the opposite reactions, i.e. oxidation of $Fe(s)$ to $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ will be of the same magnitude but with opposite sign, i.e. positive..



Thus, the free energy changes for oxidation of metallic iron $Fe^{\circ}(s)$ will be negative in both these reactions:

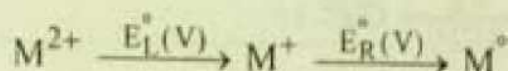
$$\Delta G_{02}^{\circ} = -2FE_{02}^{\circ} = -2 \times 96500 \times 0.44 \text{ V.C.mol}^{-1} = -84.9 \text{ kJmole}^{-1}$$

$$\Delta G_{03}^{\circ} = -3FE_{03}^{\circ} = -3 \times 96500 \times 0.04 \text{ V.C.mole}^{-1} = -11.6 \text{ kJ.mole}^{-1}$$

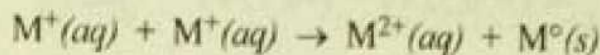
Although the free energy change for the transformation of $Fe^{\circ}(s)$ to $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$ are negative, but the free energy change for the transformation to $Fe^{2+}(aq)$ is more negative than that for the transformation to $Fe^{3+}(aq)$. That is why, metallic iron dissolves in acid in the $Fe^{2+}(aq)$ form not in the $Fe^{3+}(aq)$ form.

Latimer diagrams are also useful in predicting disproportionation and comproportionation

reactions of an element. Consider the following Latimer diagram of a metallic element M:



For spontaneous disproportionation of the intermediate oxidation state species $M^+(aq)$ in aqueous solution to solid metal $M^\circ(s)$ and $M^{2+}(aq)$ ion according to the overall reaction,

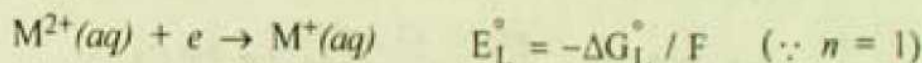


the free energy change (ΔG°) of the reaction should be negative, so the standard potential (E°) of the overall reaction should be positive ($\because \Delta G^\circ = -nFE^\circ$). The overall reaction maybe expressed as the difference of two half-reactions in terms of the Latimer diagram:

Right hand (R) couple:



Left hand (L) couple:



Free energy change (ΔG°) of the overall disproportionation reaction will be the algebraic difference of the free energy change of the reaction proceeding to left (L) from that of the reaction proceeding to right (R).

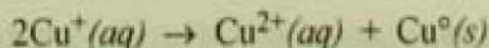
$$\begin{aligned} \Delta G^\circ &= -1.F.E^\circ = (\Delta G_R^\circ - \Delta G_L^\circ) \\ &= (-1.F.E_R^\circ) - (-1.F.E_L^\circ) \\ &= F(E_L^\circ - E_R^\circ) \\ \therefore E^\circ &= E_R^\circ - E_L^\circ \end{aligned}$$

Thus, the standard potential (E°) of the overall disproportionation reaction will be positive (hence, ΔG° negative), if the standard potential of the right hand couple is higher than that of the left hand couple ($E_R^\circ > E_L^\circ$). Therefore, an intermediate oxidation number species of an element in a Latimer diagram will have a thermodynamic tendency to disproportionate to its two neighbouring oxidation states, if the standard potential on the right of the species is higher than the potential on its left.

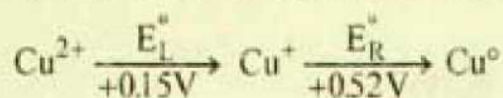
Examples (2.48)

(1) $Cu^+(aq)$ disproportionates to $Cu^{2+}(aq)$ and Cu metal.

The overall disproportionation reaction is,



The Latimer diagram of copper involving these species in 1 M acid medium is,



$$E_R^\circ (+0.52\text{V}) > E_L^\circ (+0.15\text{V})$$

$$E^\circ = E_R^\circ - E_L^\circ = (+0.52\text{V}) - (+0.15\text{V}) = +0.37\text{V}$$

Since E° for the overall reaction is positive, therefore, ΔG° is negative.

So the disproportionation of Cu^+ is spontaneous. Equilibrium constant of the overall disproportionation reaction may be defined as,

$$K^\circ = \frac{[\text{Cu}^{2+}]}{[\text{Cu}^+]^2}$$

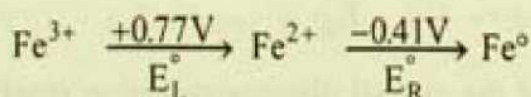
$$\Delta G^\circ = -2.303 RT \log_{10} K^\circ = -nFE^\circ$$

$$\therefore \log_{10} K^\circ = \frac{nE^\circ}{2.303RT/F} = \frac{nE^\circ}{0.059} \quad (\text{at } 25^\circ\text{C})$$

$$\begin{aligned} \therefore K^\circ &= 10^{E^\circ/0.059} = 10^{0.37/0.059} \approx 10^{6.27} \\ &= 1.87 \times 10^6 \quad (\text{at } 25^\circ\text{C}) \\ &(\because n = 1) \end{aligned}$$

(2) $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+})$ and $E^\circ(\text{Fe}^{2+}/\text{Fe}^\circ)$ couples are +0.77V and -0.41V respectively. Predict the probability of disproportionation of Fe^{2+} under standard condition.

The Latimer diagram for the three iron species is,

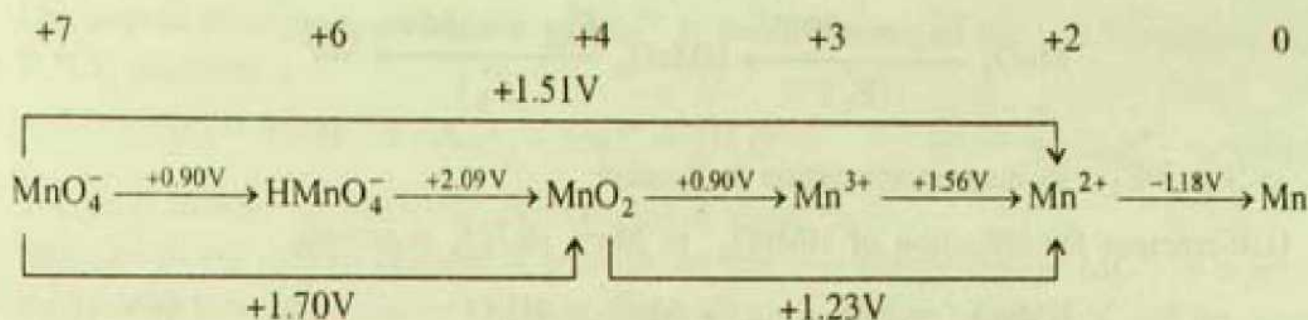


$$\therefore E_R^\circ < E_L^\circ \text{ and } (E_R^\circ - E_L^\circ) = (-0.41 - 0.77)\text{V} = -1.18\text{V} \text{ (negative)}$$

$\therefore E^\circ$ of the overall reaction is negative, so free energy change is positive, therefore, Fe^{2+} will not spontaneously disproportionate under standard condition. Even if it does so, according to the overall reaction: $3\text{Fe}^{2+} \rightarrow 2\text{Fe}^{3+} + \text{Fe}^\circ$, involving 2 electrons, for each of the half-reactions ($\text{Fe}^{2+} + 2e \rightarrow \text{Fe}^\circ$ and $2\text{Fe}^{3+} + 2e \rightarrow 2\text{Fe}^{2+}$), the equilibrium constant (K°) of the reaction at 25°C will be negligibly small.

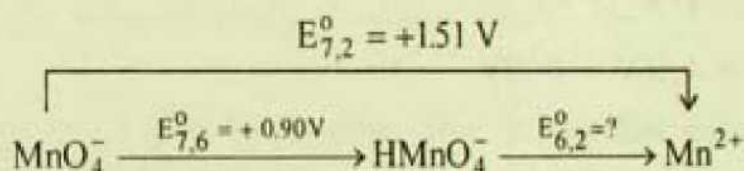
$$[K^\circ = 10^{nE^\circ/0.059} = 10^{2 \times (-1.18)/0.059} = 10^{-40}]$$

(3). Consider the Latimer diagram of manganese in 1M acidic solution.



- (i) Indicate whether Mn(VI) ions are stable or unstable toward disproportionation to Mn(VII) and Mn (II) ions in acidic solution.
- (ii) Comment on the redox stability of Mn(III) ion.
- (iii) Can MnO_2 spontaneously disproportionate to Mn(II) and Mn(VII) ions?

(i) The part of the Latimer diagram of Mn involving Mn(VII), Mn(VI) and Mn(II) ions may be cut out from the main diagram.



Standard potentials for reduction of MnO_4^- to HMnO_4^- and MnO_4^- to Mn^{2+} in acid medium are:

$$E_{\text{MnO}_4^-/\text{Mn}^{2+}}^{\circ} = E_{7,2}^{\circ} = +1.51\text{V}$$

$$E_{\text{MnO}_4^-/\text{HMnO}_4^-}^{\circ} = E_{7,6}^{\circ} = +0.90\text{V}$$

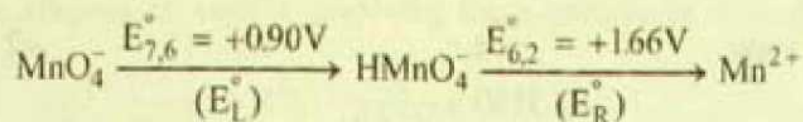
But standard potential for reduction of HMnO_4^- to Mn^{2+} ion i.e., $E_{\text{HMnO}_4^-/\text{Mn}^{2+}}^{\circ} = E_{6,2}^{\circ}$ is not provided on the Latimer diagram, but it can be calculated from the standard potentials of the other two couples i.e. $E_{7,2}^{\circ}$ and $E_{7,6}^{\circ}$ using the relation (cf. p-172),

$$E_{7,2}^{\circ} \text{ V} = \frac{(7-6)E_{7,6}^{\circ} + (6-2)E_{6,2}^{\circ}}{(7-2)}$$

$$1.51 \text{ V} = \frac{+0.90 + 4E_{6,2}^{\circ}}{5}$$

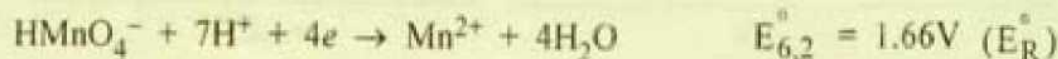
$$\therefore E_{6,2}^{\circ} = [(5 \times 1.51 - 0.90)/4] \text{ V} = 1.66\text{V}$$

Now put the E° values of the two redox couples involving the Mn(VI) species in yet another simpler form of the Latimer diagram:

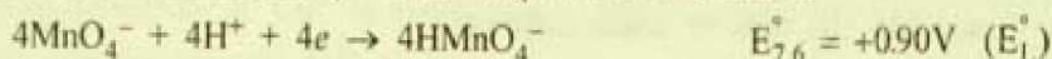


$\therefore E_R^\circ > E_L^\circ$, so disproportionation will occur.

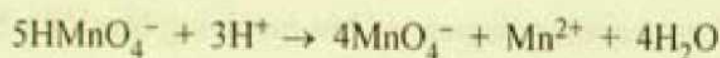
Half-reaction for reduction of HMnO_4^- to Mn^{2+} (R.H.S. reaction),



Half-reaction for reduction of MnO_4^- to HMnO_4^- (L.H.S. reaction),



The overall disproportionation reaction will be the difference of the L.H.S. reaction from the R.H.S. reaction and the number of electrons transferred (n) will be equal to 4.



$$E^\circ = (E_R^\circ - E_L^\circ)$$

$$= 1.66\text{V} - 0.90\text{V}$$

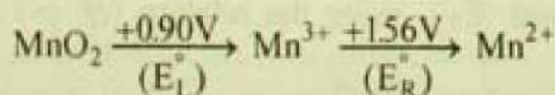
$$= +0.76\text{V}$$

Since the standard potential of the RHS couple (E_R°) is greater than that of the LHS couple (E_L°), disproportionation of Mn(VI) will occur. Since standard potential E° of the overall reaction is positive, therefore, free energy change (ΔG°) of the overall reaction is negative. So the disproportionation reaction of HMnO_4^- to MnO_4^- and Mn^{2+} ions in acid medium will be spontaneous.

The equilibrium constant (K°) of the overall reaction at 25°C will be,

$$K^\circ = 10^{nE^\circ/0.059} = 10^{4 \times 0.76/0.059} = 10^{51.5} = 3.35 \times 10^{51}$$

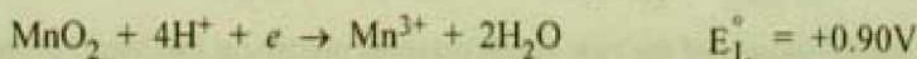
(ii) For MnO_2 , Mn^{3+} and Mn^{2+} species the simplified Latimer diagram in acid medium is,



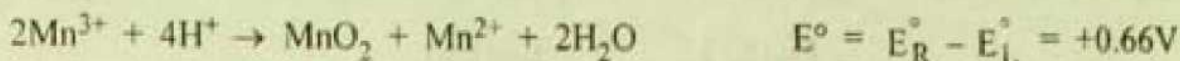
Since $E_R^\circ > E_L^\circ$ and $(E_R^\circ - E_L^\circ)$ is positive, disproportionation of Mn^{3+} to MnO_2 and Mn^{2+} will occur spontaneously. The half-reaction for reduction of Mn^{3+} (R.H.S. reaction) is,



and the half-reaction for oxidation of Mn^{3+} to MnO_2 (L.H.S. reaction) is,



The overall disproportionation reaction of Mn^{3+} is the difference of the L.H.S. reaction from the R.H.S. reaction,

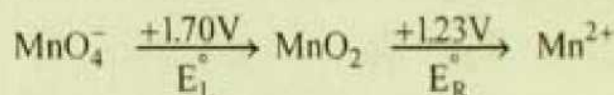


The total number of electrons involved (n) is equal to 1.

Since E° of the overall reaction is positive, so, the free energy change (ΔG°) is negative, and the disproportionation reaction is spontaneous. The equilibrium constant (K°) of the overall reaction at 25°C will be,

$$\begin{aligned} K^\circ &= 10^{nE^\circ/0.059} = 10^{1 \times 0.66/0.059} \\ &= 10^{11.2} \\ &\approx 1.54 \times 10^{11} \end{aligned}$$

(iii) The part of the simplified Latimer diagram involving MnO_4^- , MnO_2 and Mn^{2+} in acid medium may be presented as,

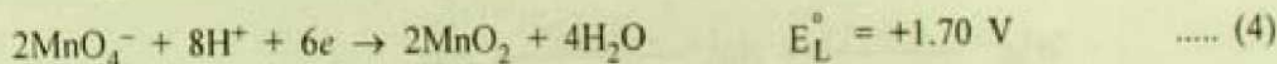
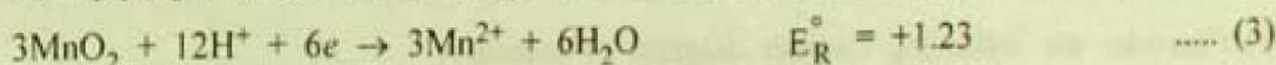


$\therefore E_R^\circ < E_L^\circ$, ($E_R^\circ - E_L^\circ$) will be negative. That is the standard potential (E°) of the overall reaction will be negative, hence the free energy change will be positive. Therefore, MnO_2 will not spontaneously disproportionate.

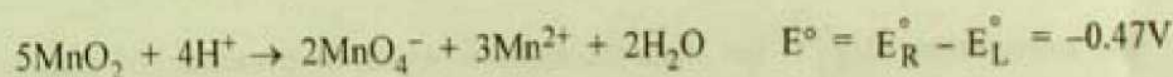
Reduction and oxidation half-reactions of MnO_2 for this disproportionation should be (1) and (2) respectively,



Multiplying (1) by 3 and (2) by 2, one obtains equations (3) and (4) respectively,



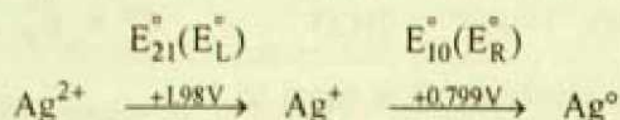
Thus, each half-cell reaction involves 6 electrons for balancing. The overall reaction is obtained from the difference (3) - (4):



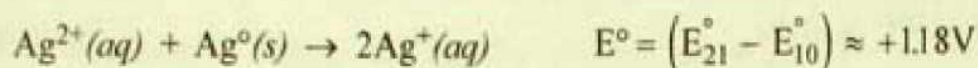
Equilibrium constant (K°) of the reaction at 25°C will be negligibly small,

$$\begin{aligned} K^\circ &= 10^{nE^\circ/0.059} = 10^{6 \times (-0.47)/0.059} \\ &= 10 \approx 1.6 \times 10^{-48} \end{aligned}$$

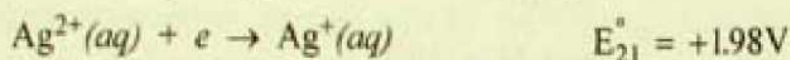
(4) Consider the Latimer diagram of silver given below and predict the probability of comproportionation of $\text{Ag}^{2+}(\text{aq})$ ion and $\text{Ag}^{\circ}(\text{s})$ to $\text{Ag}^{+}(\text{aq})$ ion.



The overall comproportionation reaction between $\text{Ag}^{2+}(\text{aq})$ and Ag° is,



This overall reaction may be splitted into two component half-reactions:



At equilibrium, potential of the two couples will be the same:

$$E_{21} = E_{10}$$

$$\therefore E_{21}^{\circ} + 0.059 \log_{10} \frac{[\text{Ag}^{2+}]}{[\text{Ag}^{+}]} = E_{10}^{\circ} + 0.059 \log_{10} [\text{Ag}^{+}]$$

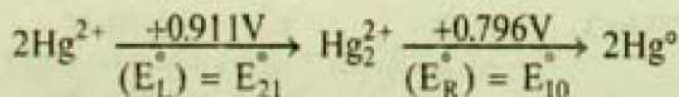
$$\therefore (E_{21}^{\circ} - E_{10}^{\circ}) = 0.059 \log_{10} \frac{[\text{Ag}^{+}]^2}{[\text{Ag}^{2+}]} = 0.059 \log_{10} K^{\circ} \text{ (in dilute solution)}$$

$$\therefore \log_{10} K^{\circ} = (E_{21}^{\circ} - E_{10}^{\circ}) / 0.059 = +1.18 / 0.059$$

$$\therefore K^{\circ} = 10^{1.18/0.059} = 10^{20} \text{ at } 25^{\circ}\text{C}.$$

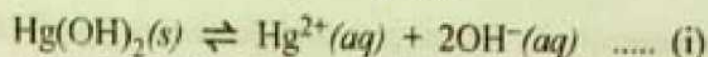
As the equilibrium constant is very large positive, so comproportionation of Ag^{2+} and Ag° to Ag^{+} ion will be spontaneous under standard condition.

(5) Consider the following Latimer diagram of mercury:

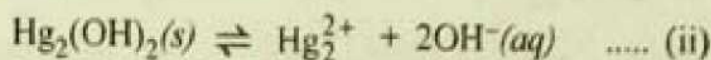


Since $E_R^{\circ} < E_L^{\circ}$, disproportion of Hg_2^{2+} to Hg^{2+} and Hg° should not be spontaneous.

Contrary to this expectation, Hg_2^{2+} ion disproportionates even in presence of traces of ammonia solution or dilute NaOH solution. This is due to the fact that, in presence of a base, both Hg^{2+} and Hg_2^{2+} ions tend to hydrolyze to form sparingly soluble hydroxides, $\text{Hg}(\text{OH})_2$ and $\text{Hg}_2(\text{OH})_2$ respectively. But the solubility of $\text{Hg}(\text{OH})_2$ is much lower than that of $\text{Hg}_2(\text{OH})_2$:



$$(K_{sp})_2 = [\text{Hg}^{2+}][\text{OH}^-]^2 = 3.1 \times 10^{-26} \quad (\text{at } 25^\circ\text{C}) \quad \therefore p(K_{sp})_2 = 25.5$$



$$(K_{sp})_1 = [\text{Hg}_2^{2+}][\text{OH}^-]^2 = 1.6 \times 10^{-23} \quad (\text{at } 25^\circ\text{C}) \quad \therefore p(K_{sp})_1 = 22.8$$

pH of precipitation of the two hydroxides may be calculated as follows:

For $\text{Hg}(\text{OH})_2$: According to solubility equilibria (i), in a saturated solution of $\text{Hg}(\text{OH})_2$,

$$[\text{OH}^-] = 2[\text{Hg}^{2+}] \quad \therefore [\text{Hg}^{2+}] = \frac{[\text{OH}^-]}{2}$$

$$\therefore (K_{sp})_2 = [\text{Hg}^{2+}][\text{OH}^-]^2 = \frac{[\text{OH}^-]}{2} \cdot [\text{OH}^-]^2 = \frac{[\text{OH}^-]^3}{2}$$

$$\therefore [\text{OH}^-]^3 = 2(K_{sp})_2$$

$$\therefore \left(\frac{K_w}{[\text{H}^+]} \right)^3 = 2 \cdot (K_{sp})_2$$

$$\frac{1}{[\text{H}^+]^3} = \frac{2 \cdot (K_{sp})_2}{(K_w)^3} = \frac{2 \times 3.1 \times 10^{-26}}{(10^{-14})^3} = 6.2 \times 10^{16}$$

$$\therefore \text{pH} \approx 5.6$$

For $\text{Hg}_2(\text{OH})_2$: According to solubility equilibria (ii), in a saturated solution of $\text{Hg}_2(\text{OH})_2$

$$[\text{OH}^-] = 2[\text{Hg}_2^{2+}] \quad \therefore [\text{Hg}_2^{2+}] = \frac{[\text{OH}^-]}{2}$$

$$\therefore (K_{sp})_1 = [\text{Hg}_2^{2+}][\text{OH}^-]^2 = \frac{[\text{OH}^-]}{2} \cdot [\text{OH}^-]^2$$

$$= \frac{[\text{OH}^-]^3}{2} = \frac{(K_w / [\text{H}^+])^3}{2}$$

$$\therefore \frac{1}{[\text{H}^+]^3} = \frac{2 \cdot (K_{sp})_1}{(K_w)^3} = \frac{2 \times 1.6 \times 10^{-23}}{(10^{-14})^3} = 3.2 \times 10^{19}$$

$$\therefore \text{pH} = 6.50$$

Therefore, $\text{Hg}(\text{OH})_2$ precipitates at comparatively lower pH than $\text{Hg}_2(\text{OH})_2$. As a result of precipitation of $\text{Hg}(\text{OH})_2$, the concentration of the oxidant component of the $2\text{Hg}^{2+}/\text{Hg}_2^{2+}$

redox couple is lowered, consequently its formal potential decreases significantly. For the half-reaction,



the Nernst equation is,

$$E_{21} = E_{21}^\circ + \frac{0.059}{2} \log \frac{[\text{Hg}^{2+}]^2}{[\text{Hg}_2^{2+}]}$$

In between pH 5.6 to 6.5 the total concentration of Hg_2^{2+} ion $(C_{\text{Hg}_2^{2+}})$ remains as free Hg_2^{2+} ion in solution, whereas, the concentration of free Hg^{2+} ion is controlled by its solubility equilibrium (i):

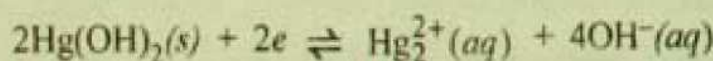
$$[\text{Hg}^{2+}] = \frac{(K_{sp})_2}{[\text{OH}^-]^2}$$

Substituting this value of $[\text{Hg}^{2+}]$ in the Nernst equation, we obtain,

$$\begin{aligned} E &= E_{21}^\circ + \frac{0.059}{2} \log \frac{\{(K_{sp})_2 / [\text{OH}^-]^2\}^2}{C_{\text{Hg}_2^{2+}}} \\ &= E_{21}^\circ + \frac{0.059}{2} \log \left[\frac{(K_{sp})_2 [\text{H}^+]^2}{K_w^2} \right] - \frac{0.059}{2} \log C_{\text{Hg}_2^{2+}} \\ &= E_{21}^\circ + \frac{0.059}{2} \times 2 \log \frac{(K_{sp})_2 [\text{H}^+]^2}{K_w^2} - 0.0295 \log C_{\text{Hg}_2^{2+}} \\ &= \left(E_{21}^\circ - 0.059 p(K_{sp})_2 + 0.118 pK_w - 0.118 p[\text{H}] - 0.0295 \log C_{\text{Hg}_2^{2+}} \right) \\ &= \left(E_{21}^f - 0.0295 \log C_{\text{Hg}_2^{2+}} \right) \text{V} \end{aligned}$$

where, $E_{21}^f = E_{21}^\circ - 0.059 p(K_{sp})_2 + 0.118 pK_w - 0.118 p[\text{H}]$,

which is the formal potential of the half-reaction,



that dominates in the solution in the pH range, $5.6 < \text{pH} < 6.5$ where, $\text{Hg}(\text{OH})_2$ starts precipitating, but $\text{Hg}_2^{2+}(aq)$ remains in solution. The formal potential (E_{21}^f) of the system at $p[\text{H}]$ 5.6 is,

$$E_{21}^f = (0.911 - 0.059 \times 25.5 + 0.118 \times 14 - 0.118 \times 5.6)V$$

$$\approx 0.40V.$$

This formal potential (E_{21}^f) of the $2\text{Hg}(\text{OH})_2/\text{Hg}_2^{2+}$ couple is now the formal potential (E_L^f) of the L.H.S. couple of Hg_2^{2+} ion in the Latimer diagram of mercury. Since E_R° (+0.796V i.e. E_{10}°) is now greater than E_L^f (+0.40V, i.e. E_{21}^f), that is why, Hg_2^{2+} ion disproportionates to Hg^{2+} ion and $\text{Hg}^\circ(l)$ under this condition. This reaction forms the basis of qualitative identifying test of mercurous mercury with *aq*- NH_3 solution, in which mercurous salts are transformed to black metallic mercury and Hg^{2+} ion (cf. Sect. 4.3).

(ii) Frost diagrams

Frost diagram (or, oxidation state diagram) of an element shows the relative free energy, rather than potential, on the vertical axis and the oxidation states on the horizontal axis. Transformation of an element X from its oxidation number ($\pm n$) to its elemental state of zero (0) oxidation number may be represented by the half-reaction,

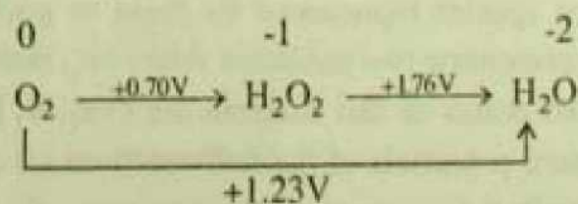


The quantity, $nE^\circ(V)$, called the *volt equivalent* of the $\text{X}(\pm n)/\text{X}(0)$ redox couple is proportional to the standard free energy change (ΔG°) for the conversion of $\text{X}(\pm n)$ to $\text{X}(0)$,

$$nE^\circ = -\Delta G^\circ/F$$

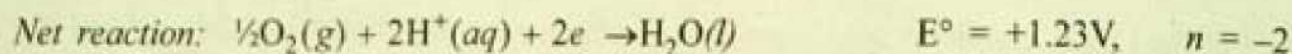
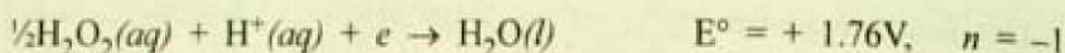
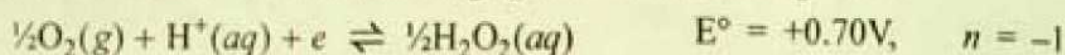
Frost diagram of the element X is the plot of $-nE^\circ$ of the redox couples $\text{X}(\pm n)/\text{X}(0)$ for various oxidation numbers ($\pm n$) of the element X against ($\pm n$). The quantity $-nE^\circ$ of a redox step is expressed in units of volts times moles of electrons for this step ($V.mol.^{-1}.e$). We obtain the same value by dividing the free energy change (ΔG°) with Faraday constant F (i.e. $\Delta G^\circ/F$). The element in the oxidation state zero (0) is considered to have zero free energy. The ($n, -nE^\circ$) data of the successive oxidation states on joining by straight lines, produce the Frost diagram of the element. The oxidation numbers of the element are plotted on the horizontal axis with zero at the middle, positive oxidation numbers on the R.H.S. and negative oxidation numbers on the L.H.S. or vice-versa in the increasing orders. Most stable oxidation state of an element lies lowest in the Frost diagram.

Frost diagram of an element maybe constructed from its Latimer diagram. Consider the following Latimer diagram of oxygen:



Oxidation numbers of oxygen in this diagram are 0 in O_2 , -1 in H_2O_2 and -2 in H_2O .

The first point, i.e., for O_2 is zero, since $-nE^\circ = 0$. Considering changes per mole of O-atoms, the half-reactions for conversion of oxygen to H_2O_2 and oxygen to H_2O are :



Thus, the (n, nE°) coordinates for H_2O_2 are $n = -1$, $nE^\circ = -0.70V$ and those for H_2O are $n = -2$, $nE^\circ = -2.46$, since free energy of oxygen in H_2O molecule will be $-(1 \times 1.76)$ units below that of the H_2O_2 point. Now joining the three (n, nE°) coordinates by straight lines, we obtain the Frost diagram of oxygen in acid solution (Fig 2.4).

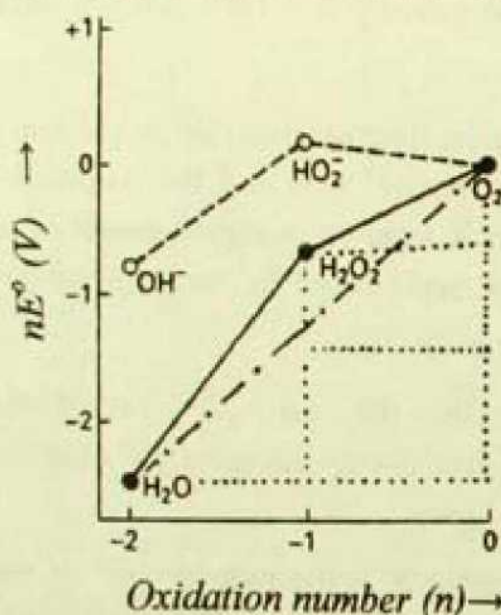
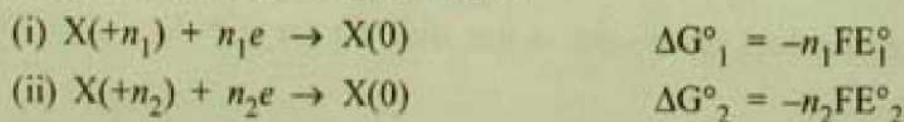


Fig. 2.4. Frost diagram of O_2 . ●—● acidic solution, 0----0 basic solution, ... free energy changes, ——— convex curve (disproportionation of H_2O_2).

Frost diagrams give a visual image of the redox chemistry of the element. Water occurs at the lowest point in the Frost diagram of oxygen, indicating that the oxidation state (-2) of oxygen in water is thermodynamically the most stable state of oxygen. Hydrogen peroxide occurs on a *convex curve*, which indicates its instability toward *disproportionation*. Similarly, occurrence of a species on a *concave curve* in the Frost diagram indicates its instability toward *comproportionation reaction* (cf. Fig. 2.6).

One of the very exciting features of Frost diagram is that, the slope of the straight line connecting the two points on a Frost diagram is equal to the standard potential of the redox couple formed by the two species represented by these two points. Consider a part of a Frost diagram (Fig. 2.5) representing two oxidation states $+n_1$ and $+n_2$ of the element X ($n_2 > n_1$). The coordinates of the two points in this diagram are $(+n_1, n_1 E_1^\circ)$ and $(+n_2, n_2 E_2^\circ)$, where, E_1° and E_2° are the standard potentials of the half-reactions (i) and (ii), and, ΔG_1° and ΔG_2° are the corresponding standard free energy changes:



The standard free energy change (ΔG_{21}°) for reduction of the species $X(+n_2)$ to the species $X(+n_1)$ will be the difference of the standard free energy changes for reduction of $X(+n_1)$ to $X(0)$ from that of reduction of $X(+n_2)$ to $X(0)$. Omitting the (+) sign on the oxidation states for simplicity, one may write,



where, E_{21}° is the standard potential of the redox couple $X(n_2)/X(n_1)$.

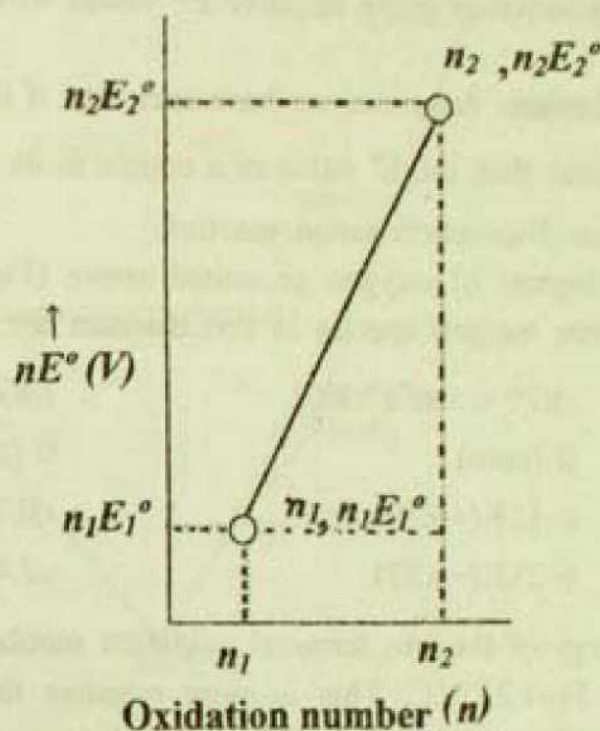


Fig. 2.5 Relation between standard potentials of redox couples and slope of straight line connecting them in their Frost diagram.

$$\text{Since, } \Delta G_{21}^{\circ} = \Delta G_2^{\circ} - \Delta G_1^{\circ} = (-n_2 F E_2^{\circ}) - (-n_1 F E_1^{\circ}) = F(n_1 E_1^{\circ} - n_2 E_2^{\circ})$$

$$\therefore E_{21}^{\circ} = \frac{n_2 E_2^{\circ} - n_1 E_1^{\circ}}{n_2 - n_1}$$

which is also the slope of the straight line joining the two points $(n_2, n_2 E_2^{\circ})$ and $(n_1, n_1 E_1^{\circ})$ in the Frost diagram. Thus, steeper is the line joining two $(n, n E^{\circ} V)$ points in a Frost diagram, higher is the reduction potential of the corresponding redox couple.

In the Frost diagram of oxygen (Fig 2.4), the $n E^{\circ} V$ and $(n, n E^{\circ} V)$ coordinates of oxygen atom in H_2O_2 and H_2O molecules are :

	n	$E^{\circ}(V)$	$(n, n E^{\circ} V)$
H_2O	$n_1 = -2$	$E_2^{\circ} + 1.23$	$(-2, -2.46)$
H_2O_2	$n_2 = -1$	$E_2^{\circ} + 0.70$	$(-1, -0.70)$

Therefore, the slope of the straight line joining the points $(-2, -2.46V)$ and $(-1, -0.70V)$ is $+1.76V$, which is the E° for the half-reaction for reduction of H_2O_2 to H_2O according to



$$E^\circ = +1.76\text{V}$$

$$\frac{n_2 E_2^\circ - n_1 E_1^\circ}{n_2 - n_1} = \frac{(-0.70)\text{V} - (-2.46)\text{V}}{(-1) - (-2)} = +1.76\text{V}$$

The oxidant component of a couple with higher positive slope (higher positive E° value) will be susceptible to undergo reduction. Similarly, the reductant component of a couple with less positive slope (less positive or more negative E° value) will be susceptible to undergo oxidation.

In the discussion on Latimer diagrams, we have seen that if the E° value of a couple on R.H.S. of a species is greater than the E° value of a couple to its L.H.S, i.e. (i.e. $E_R^\circ > E_L^\circ$) then the species undergoes disproportionation reaction.

Consider the Frost diagram of oxygen presented above (Fig. 2.4). Gibbs free energy ($\Delta G^\circ = -nFE^\circ$) of the three oxygen species in this diagram are:

Species	$\Delta G^\circ = -nFE^\circ(\text{V.C})$	$(\Delta G^\circ/F) = -nE^\circ(\text{V})$
O_2	0 (zero)	0 (zero)
H_2O_2	$(-1).F.(+0.70)$	-0.70
H_2O	$(-2).F.(+1.23)$	-2.46

Mean of the free energy of the two terminal oxidation number species (O_2 and H_2O) is $F[0 + (-2.46)] \text{ V.C}/2 = F(-1.23)\text{V.C}$. This is more negative than the free energy of the intermediate oxidation number species H_2O_2 . Therefore, the two straight lines joining the (n , nE°) coordinates of (O_2 and H_2O_2) and (H_2O_2 and H_2O) will intersect at H_2O_2 point forming a convex curve (Fig. 2.4). Therefore, it may be generalized that 'a thermodynamically unstable species is located at a *convex curve* in the Frost diagram and such a species can undergo *disproportionation*'.

Similarly, when the free energy of an intermediate oxidation state species becomes lower than the mean of the free energies of the two terminal species, then the intermediate oxidation state is thermodynamically more stable. 'When an intermediate oxidation number species is thermodynamically more stable than the two terminal oxidation state species, the two terminal species may undergo *comproportionation* to the intermediate oxidation state species. Such an intermediate oxidation state species is located at a *concave curve* on the Frost diagram'.

Although a given species may be thermodynamically unstable toward redox reaction, kinetics of such reactions are often slow, particularly when there is a phase change. Although H_2O_2 is thermodynamically unstable toward disproportion to H_2O and O_2 gas, the reaction is kinetically quite slow and that is why H_2O_2 can be prepared and stored in the laboratory at ordinary temperature.

In a Frost diagram, thermodynamically stable species are located at the bottom. The lower is the position of a species in the Frost diagram, thermodynamically more stable it is toward redox reaction. Any species located at the upper right side of the diagram will be an oxidizing

agent. Similarly, any species located at the lower left side of the Frost diagram will be a reducing agent (if the positive oxidation numbers are plotted on the R.H.S. and the negative oxidation numbers on the L.H.S.)

Almost all the features of Frost diagrams are reflected in the Frost diagram of manganese (Fig. 2.6).

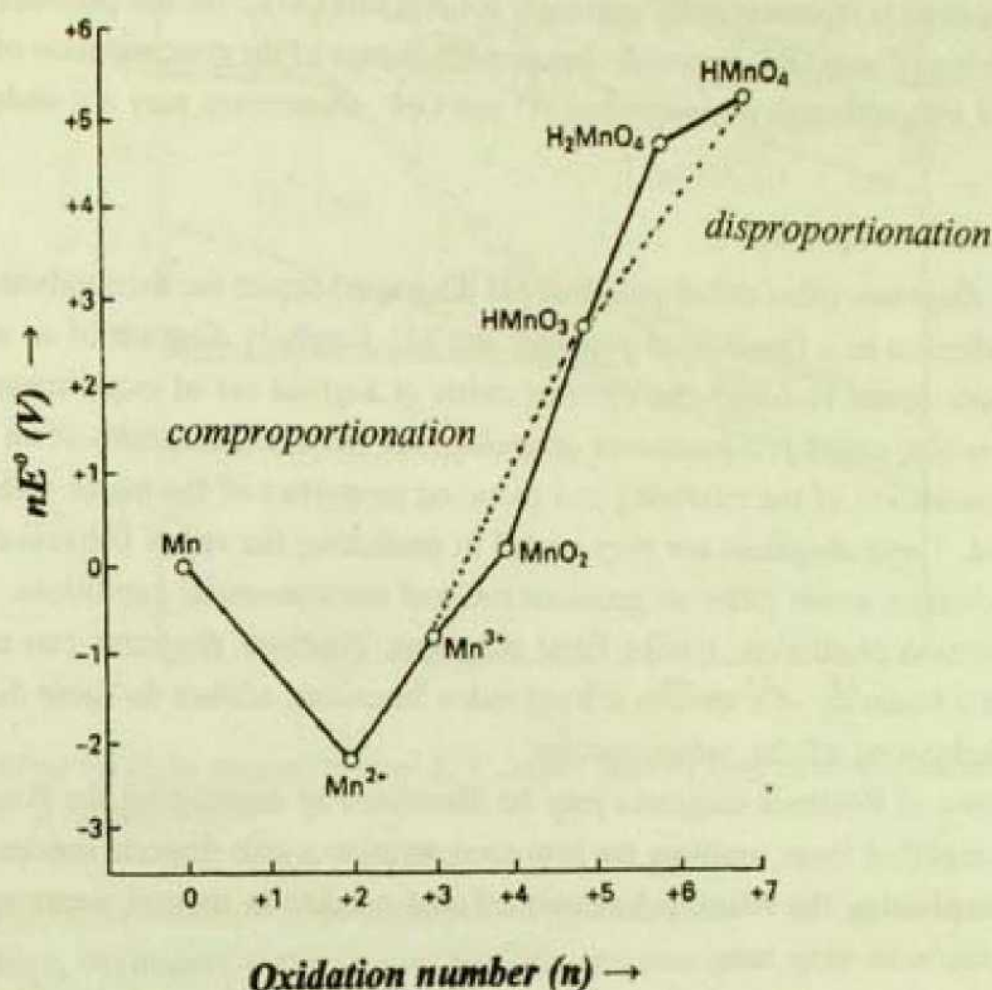


Fig. 2.6. Simplified Frost diagram of manganese in acid medium.

- (i) Mn^{2+} ion is located at the bottom of the diagram. It is the thermodynamically most stable form of manganese.
- (ii) MnO_4^- ion is located at the upper right of the diagram. It is a very strong oxidizing agent. But its reduction to Mn^{2+} is kinetically slow, except in presence of a catalyst and that is why, permanganate solution can be stored and used as a reagent in the laboratory.
- (iii) Mn metal, located at the lower left of the diagram, is a mild reducing agent.
- (iv) Manganate (MnO_4^{2-}) and Mn^{3+} ions are located at *convex points* on the Frost diagram. These ions are unstable toward *disproportionation*.
- (v) MnO_2 occurs on a *concave point* and it does not disproportionate. On the other hand, the two terminal species Mn^{3+} and HMnO_3 may undergo *comproportionation* to MnO_2 .

Frost diagrams only give information about the redox behaviours of the species in 1M acid ($pH = 0$) and 1 M base ($pH = 14$). Nature of the species and also their thermodynamic stabilities may be different in the intermediate pH ranges. As for example, in a Frost diagram of manganese under basic condition, the most stable species Mn^{2+} does not occur, instead the +2 oxidation state of the element is represented by sparingly soluble $Mn(OH)_2$. Formal potential of any redox process involving H^+ and OH^- ions will change with change of the concentration of these species (i.e. change of pH), although these species, H^+ and OH^- , themselves may not undergo oxidation or reduction.

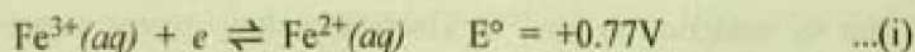
(iii) Pourbaix diagrams

Pourbaix diagrams (also called potential- pH diagrams) depict the thermodynamically stable forms of an element as a function of potential and pH . Pourbaix diagram of an element shows the predominate forms in which the element exists at a given set of experimental conditions. Therefore, it is also called *predominance area diagram*. Pourbaix diagrams of an element gives a visual representation of the oxidizing and reducing properties of the major stable compounds of the element. These diagrams are very useful in predicting the redox behaviours of different forms of an element under different geochemical and environmental conditions. They are also useful in corrosion prediction. Unlike Frost diagrams, Pourbaix diagrams can not predict the thermodynamic tendency of a species toward redox reactions, neither do these diagrams reflect any kinetic behaviour of the redox species.

Applications of Pourbaix diagrams may be illustrated by developing the Pourbaix diagram of iron in a simplified form, omitting the low concentration μ -oxo dimeric species. The diagram is useful in explaining the redox behaviours of iron species in natural water systems, where iron concentration is very low.

We can start from acidic solution ($[H^+] = 1M$, $p[H] = 0$) and proceed to higher pH values upto $p[H] = 14$ ($[OH^-] = 1M$), considering only two oxidation states (+3 and +2) species of iron.

In acid medium ($p[H] = 0$), the major iron species are $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ ions and the reduction half-reaction is,



Since this half-reaction does not involve H^+ ion, so its potential will be independent of pH (ignoring the effect of H^+ ion on the activities of $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ ions). A plot of $E^\circ(V)$ against $p[H]$ for this half-reaction will be a horizontal straight line parallel to the $p[H]$ axis (Fig 2.7). $Fe^{2+}(aq)$ may be oxidized to $Fe^{3+}(aq)$ by redox couples having redox potentials higher than that represented by this horizontal line and $Fe^{3+}(aq)$ may be reduced to $Fe^{2+}(aq)$ by redox couples having redox potentials lower than that represented by this horizontal line. This horizontal line near the top left of this diagram represents the boundary that separates the regions where $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ ions predominate.

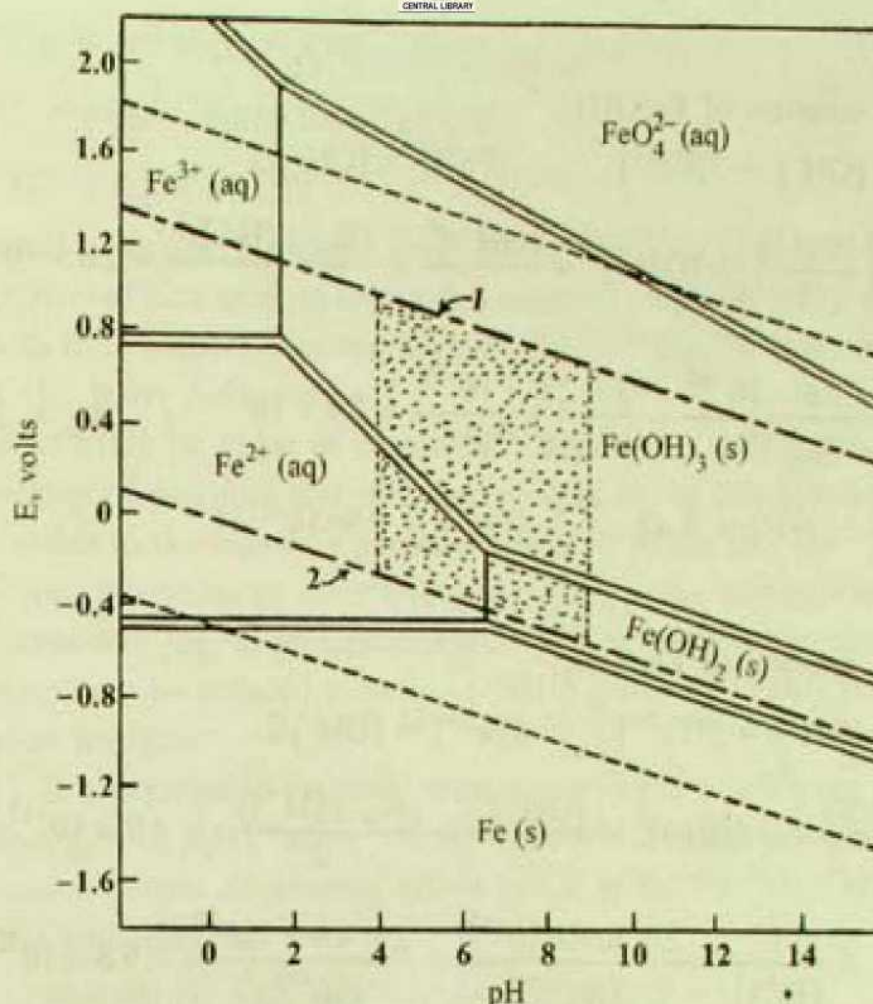
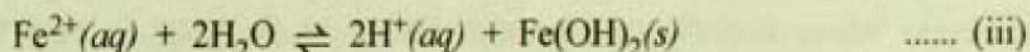
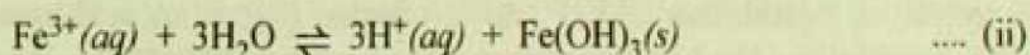
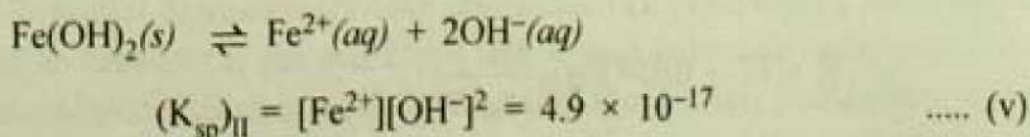
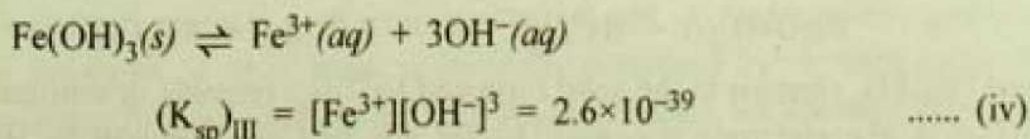


Fig. 2.7. Simplified Pourbaix diagram of iron. 1, 2 : redox stability field of water, shaded region : $p[H]$ ranges in natural waters.

As the $p[H]$ is increased, the possibilities of hydrolysis of $Fe^{3+}(aq)$ and $Fe^{2+}(aq)$ ions gradually increase, eventually $Fe(OH)_3$ and $Fe(OH)_2$ are precipitated at different $p[H]$ values.



These are acid-base equilibria, not redox equilibria, as the oxidation numbers of iron remain the same on both sides of these equilibria. We can have an idea about the $p[H]$ of the solution at which $Fe(OH)_3$ and $Fe(OH)_2$ will precipitate, from a consideration of solubility equilibria of these two hydroxides at $25^\circ C$:



For $\text{Fe}(\text{OH})_3$:

In a saturated solution of $\text{Fe}(\text{OH})_3$,

$$[\text{OH}^-] = 3[\text{Fe}^{3+}] \quad \therefore [\text{Fe}^{3+}] = [\text{OH}^-]/3$$

$$\therefore (K_{sp})_{\text{III}} = \left(\frac{[\text{OH}^-]}{3} \right) \times [\text{OH}^-]^3 = \frac{[\text{OH}^-]^4}{3} = \frac{(K_w / [\text{H}^+])^4}{3} = 2.6 \times 10^{-39}$$

$$\therefore \frac{1}{[\text{H}^+]^4} = \frac{3 \times 2.6 \times 10^{-39}}{(K_w)^4} = \frac{3 \times 2.6 \times 10^{-39}}{(10^{-14})^4} = 7.8 \times 10^{17} \quad (\because K_w = 10^{-14})$$

$$\therefore p[\text{H}] \approx 4.42 \quad \therefore [\text{Fe}^{3+}] \approx 9.9 \times 10^{-11} \text{M}$$

For $\text{Fe}(\text{OH})_2$:

In a saturated solution of $\text{Fe}(\text{OH})_2$,

$$[\text{OH}^-] = 2[\text{Fe}^{2+}] \quad \therefore [\text{Fe}^{2+}] = [\text{OH}^-]/2$$

$$\therefore (K_{sp})_{\text{II}} = \frac{[\text{OH}^-]}{2} \times [\text{OH}^-]^2 = \frac{[\text{OH}^-]^3}{2} = \frac{(K_w / [\text{H}^+])^3}{2} = 4.9 \times 10^{-17}$$

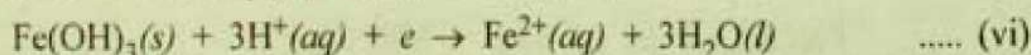
$$\therefore \frac{1}{[\text{H}^+]^3} = \frac{2 \times 4.9 \times 10^{-17}}{(K_w)^3} = \frac{2 \times 4.9 \times 10^{-17}}{(10^{-14})^3} = 9.8 \times 10^{25}$$

$$\therefore p[\text{H}] = 8.66 \quad \therefore [\text{Fe}^{2+}] \approx 2.3 \times 10^{-6} \text{M}$$

Therefore, starting from a very dilute solution containing $\text{Fe}^{3+}(\text{aq})$ and $\text{Fe}^{2+}(\text{aq})$ ions, on increase of $p[\text{H}]$ from $p[\text{H}] = 0$, $\text{Fe}(\text{OH})_3$ will start precipitating first (around at $p[\text{H}] \geq 4.4$). $\text{Fe}(\text{OH})_2$ will start precipitating next around $p[\text{H}] \geq 8.7$.

The hydrolytic equilibrium of $\text{Fe}^{3+}(\text{aq})$ ion [eqm. (ii)] is an acid-base equilibrium, and not a redox equilibrium. The boundary between the regions where $\text{Fe}^{3+}(\text{aq})$ ion remains soluble and the region where $\text{Fe}(\text{OH})_3$ precipitates, limits the $\text{Fe}^{3+}(\text{aq})$ to very low concentration ($\sim 9.9 \times 10^{-11} \text{M}$). This boundary is independent of any redox couples, but does depend upon $p[\text{H}]$. $\text{Fe}^{3+}(\text{aq})$ is favoured at $p[\text{H}]$ lower than ~ 4 , whereas, $\text{Fe}(\text{OH})_3$ is favoured at $p[\text{H}]$ higher than 4. The equilibrium concentration of $\text{Fe}^{3+}(\text{aq})$ varies with $p[\text{H}]$ and the vertical boundary line in the diagram represents the $p[\text{H}]$ at which $\text{Fe}^{3+}(\text{aq})$ is the dominant species.

The redox equilibrium above $p[\text{H}]$ 4 is the half-reaction.



Since $\text{Fe}(\text{OH})_3$ remains in the solid form and $\text{Fe}^{2+}(\text{aq})$ remains in solution in the $p[\text{H}]$ range $4 \leq p[\text{H}] \leq 8$, the electrode potential (E) for this half-reaction will be given by,

$$\begin{aligned} E &= E^\circ + 0.059 \log_{10} \frac{[\text{H}^+]^3}{[\text{Fe}^{2+}]} \\ &= E^\circ + 0.059 \times 3 \log_{10} [\text{H}^+] - 0.059 \log [\text{Fe}^{2+}] \end{aligned}$$

$$E = (E^\circ - 0.177p[H] - 0.059 \log_{10}[Fe^{2+}])V$$

$$= (E^f - 0.059 \log_{10}[Fe^{2+}])V.$$

where, $E^f = (E^\circ - 0.177 p[H])V$.

Thus, the formal potential (E^f) of the $Fe(OH)_3, H^+/Fe^{2+}(aq)$ couple is a function of $p[H]$. A plot of E^f vs. $p[H]$ will be a straight line with a negative slope (-0.177), making an intercept of $E^\circ(+0.77V)$ with the horizontal line representing the $Fe^{3+}(aq)/Fe^{2+}(aq)$ couple, around $p[H] \geq 4$, where, $Fe(OH)_3$ starts precipitating.

With increase of $p[H]$ the value of E^f gradually decreases. The oxidized species $Fe(OH)_3$ is stable in the region of potential and $p[H]$ represented above this line and the reduced form $Fe^{2+}(aq)$ is stable in the region of potential and $p[H]$ below this line. Thus, with increase of $p[H]$, the $Fe^{2+}(aq)$ ion becomes more strongly reducing. So, stronger oxidizing agent will be required to oxidize $Fe^{2+}(aq)$ to precipitate $Fe(OH)_3$ in acidic solution than in basic solution. Nitro ($-NO_2$) group may be reduced to amino ($-NH_2$) group by freshly precipitated $Fe(OH)_2$ in strongly alkaline medium.

Above $p[H] \geq 8$, precipitation $Fe(OH)_2$ starts according to equilibrium (iii), and a vertical line separates the region of $p[H]$, below which $Fe^{2+}(aq)$ dominates and above which $Fe(OH)_2$ dominates. The redox couple dominating above $p[H]8$ is the $Fe(OH)_3, H^+/Fe(OH)_2$ couple, represented by the half-reaction,



for which the redox potential (E) will be given by,

$$E = E^f + 0.059 \log_{10}[H^+]$$

$$= (E^f - 0.059 p[H])V = (E'')$$

where, (E'') is the new formal potential of the system above $p[H] 8$, and it is again a function $p[H]$. With increase of $p[H]$, formal potential of the $Fe(OH)_3, H^+/Fe(OH)_2$ couple decreases with a negative slope (-0.059), making an intercept equal to $E^f(V)$, the formal potential of the $Fe(OH)_3, 3H^+/Fe^{2+}$ couple at the point of commencement of precipitation of $Fe(OH)_2$. The line representing this $Fe(OH)_3, H^+/Fe(OH)_2$ couple has a less steep slope than the line representing the $Fe(OH)_3, 3H^+/Fe^{2+}$ couple, since smaller number of H^+ ions are involved in this case.

Thus, looking at the Pourbaix diagram of iron, we can explain why all qualitative identifying tests of iron, e.g. formation blood red coloured $Fe(SCN)^{2+}$, Prussian blue test, etc. and all reactions for quantitative estimation of iron are carried out in fairly acidic solutions.

The Pourbaix diagrams of an element is generally presented by superimposing the same with the redox stability field of water (Fig. 2.3). Redox couples with formal potentials more positive than the potential represented by the upper line (1), representing the O_2/H_2O couple may oxidize water to liberate O_2 gas and those with formal potentials more negative than the potential represented by the lower line (2), representing the H^+/H_2 couple may reduce water to liberate H_2 gas. The redox couples, of which the formal potentials lie between the upper and lower lines representing the redox stability field of water, are stable in aqueous media.

Following points should be taken into consideration while reading the Pourbaix diagram of an element.

- (1) Vertical lines separate the species that are in acid-base equilibria.
- (2) Non-vertical lines separate the species that are involved in redox equilibria.
 - (i) Horizontal lines separate the species that are in redox equilibria not involving H^+ and OH^- ions.
 - (ii) Diagonal boundaries separate the species in redox equilibria in which H^+ and or OH^- ions are involved.
 - (iii) For coupled acid-base redox equilibria, if H^+ ions are involved on the left hand side of the half-reaction representing reduction reaction of the couple, the slope of the potential vs. $p[H]$ curve on the Pourbaix diagram will be downward (ie. negative), conversely, if the H^+ ion is involved on the right hand side of the half-reaction representing reduction reaction, the potential vs. $p[H]$ plot will have an upward (i.e. positive) slope.
- (3) The region of stability of water as solvent is represented by dashed or dotted lines.
- (4) Any point on the Pourbaix diagram of an element represents the thermodynamically most stable and also most abundant form of the element at the $p[H]$ and potential represented by that point.
- (5) Strong oxidizing agents and oxidizing conditions of potentials and $p[H]$ are found at the top of the diagram. Strong oxidizing agents have lower boundaries. Permanganate ion acts as an oxidant in the entire $p[H]$ range, but it is very strongly oxidizing in acid medium. (Fig. 2.8).

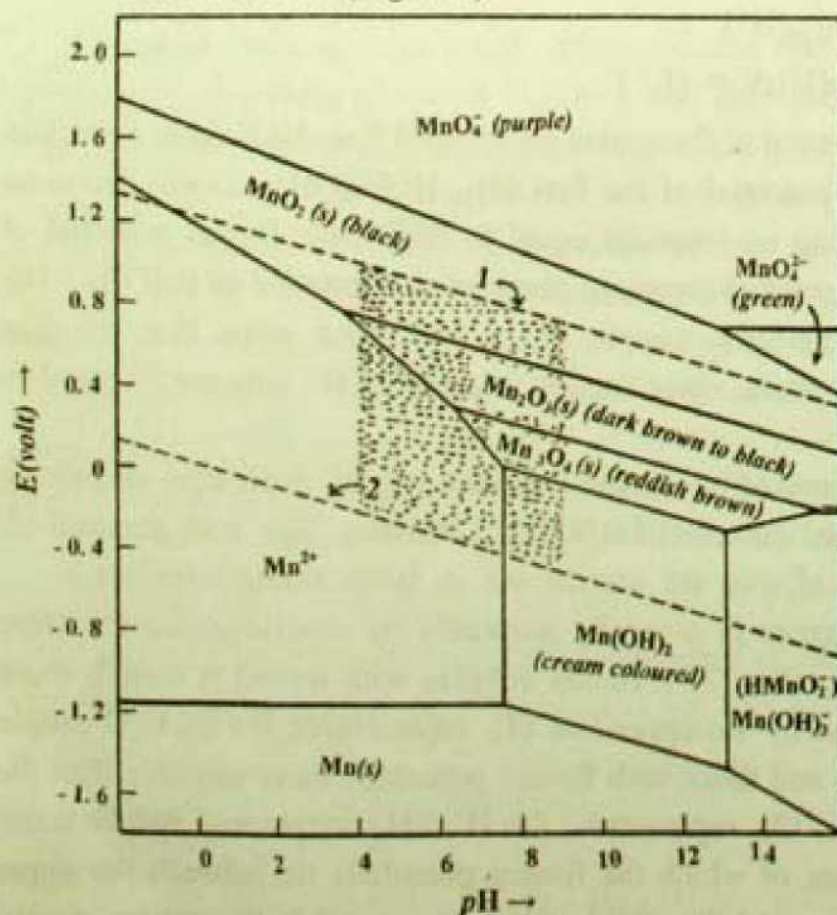


Fig. 2.8. Simplified Pourbaix diagram of manganese. 1, 2: redox stability field of water, shaded region: $p[H]$ ranges in natural waters.

- (6) Reducing agents and reducing conditions of potential and $p[H]$ occur at the bottom of the diagram. Very strong reducing agents have low upper boundaries on the diagram. Mn and Fe metals are reducing agents in the entire range of $p[H]$, and their reducing powers increase enormously in basic solutions (Figs 2.7 and 2.8).
- (7) If the predominance area of a species in an intermediate oxidation state of an element disappears completely above or below a particular $p[H]$, the species may undergo *disproportion* to its neighbouring oxidation states species.

Example (2.49)

Manganate (MnO_4^{2-}) ion is formed only in strongly alkaline condition (Fig. 2.8). It disproportionates to MnO_4^- ion and $MnO_2(s)$, if the alkalinity is lowered. In oxidative fusion test for Mn ($p -319, 458$), green coloured manganate ion is formed, when Mn(II) salts or MnO_2 is fused with caustic alkali (NaOH/KOH, or fusion mixture $Na_2CO_3 + K_2CO_3$) in presence of strong oxidant such as KNO_3 . When the green solution obtained after extracting the green fused mass with water, is treated with dilute HNO_3 , the green colour is immediately discharged and a transient pink colour due to permanganate (MnO_4^-) ion appears, which also soon disappears as MnO_4^{2-} is decomposed by the nitrite ion formed due to reduction of KNO_3 .

- (8) A species, that ranges from the top to the bottom of the Pourbaix diagram at a particular $p[H]$, will be devoid of any oxidizing and reducing properties at that pH .

2.5 Principles of Separation

(a) Chromatographic Separation

When a fluid sample or a solution is allowed to pass through a column of finely divided solid adsorbent, or a solid providing support to a liquid phase, serving as an adsorbent, then different solutes present in the sample solution partition to different extents between the stationary solid phase and the mobile fluid phase, so that bands are formed at different positions of the column. Depending upon the nature of the solute and the stationary phase, the partition process may involve surface adsorption of the solutes, distribution of the solutes between the mobile phase and a liquid phase held on a solid support, and ion-exchange. On passing a suitable fluid through the column, after addition of the sample, it is often possible to separate the bands without serious overlap, the process is called *elution*. If the separated substances are coloured, a series of coloured zones may be formed along the length of the column, when we name this type of separation as *Chromatography*. Separation by chromatography is thus based on the principle of differential adsorption/distribution.

Partition chromatography is a type of chromatographic technique in which the stationary phase is a thin film of liquid adsorbed on the surface of an inert support and the mobile phase is usually a liquid or a solution or a gas. A special type of partition chromatographic technique, known as *paper chromatography*, is often applied in qualitative inorganic analysis for separation and identification of inorganic radicals by spot test technique. The stationary phase in paper chromatography is the adsorbed water molecules present (~22%) in the filter paper, supported by the cellulose molecules of the filter paper. Usually a filter paper strip cut from a Whatman

No. 1 filter paper is spotted at the centre with the solution of the test sample by means of a capillary tube and the spot is dried in air. A drop of the specific reagent solution is added in the same manner on the sample spot, when a coloured spot is produced. The spot is dried in air as before. The paper is then held horizontally and a solution of developing or a washing liquid, specified for the test is allowed to pass on to the spot from a capillary dropper. This developing solvent serves as the mobile phase in such a manner that the solvent front moves from the centre of the spot towards the periphery of the paper strip due to *capillary action* of the filter paper. Different components of the coloured spot move at different rates. If a precipitate is formed in the spot, usually it does not move from the centre of the spot. Ionic components of the spot usually move away from the central spot with different speeds depending upon their chemical nature on application of the developing solvent. The net result is the formation of concentric coloured zones on the filter paper strip, that enable us to separate and identify the inorganic radicals. Some times the filter paper is impregnated with the reagent and the test solution is added on this reagent paper. The mobile phase is then added to create separation of the components of the mixture, followed by exposure to or treatment with developing reagents.

Examples of application of this separation technique in qualitative inorganic analysis are many:

Example (2.50)

- (i) Separation and identification of $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$ and SCN^- ions by FeCl_3 and HCl solutions (*cf.* Sect. 7.4).
- (ii) Separation and identification of Cu^{2+} and Cd^{2+} on filter paper impregnated with H_2S water or freshly precipitated ZnS slurry (*cf.* Sects. 2.2, 7.8)
- (iii) Separation and identification of MoO_4^{2-} and WO_4^{2-} by NH_4SCN , SnCl_2 and HCl solutions (*cf.* Sect. 8.9)
- (iv) Detection of Mo in presence of Fe^{III} by NH_4SCN , SnCl_2 , HCl solution (*cf.* Sect. 8.8)

The efficiency of paper chromatographic separation of ionic species may be further increased by the application of electric field (see text for electrophoresis and electrochromatography) and simultaneous application of perpendicular electric and magnetic fields (see text for magneto electrophoresis).

(b) Ion-Exchange Separation

Ion-exchange separations are often made use of in qualitative inorganic analysis, particularly for the removal of interfering ions such as phosphate. It is also useful in separating metal ions which are otherwise chemically similar but pass through ion-exchange column with different speeds.

Ion-exchange separation is done with materials called *ion exchange resins*, which are composed of cross linked structural net works, containing ionized, or, ionizable functional

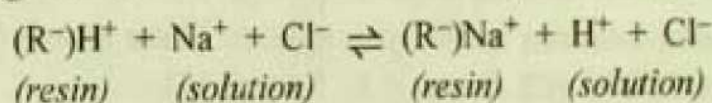
groups. These functional groups ionize to an ion fixed to the polymeric network and a *counter ion* or *active ion* in the liquid phase which can be replaced by an ion of the same charge type. Active ions in *cation exchange resins* are cations and in *anion exchange resins* the active ions are anions. Cation exchange resins contain acidic functional groups such as, $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{OH}$ (phenolic), from which H^+ ions are exchanged with cations. Anion exchange resins contain weakly basic functional groups : $-\text{NH}_2$, $-\text{NHR}$ – $\text{N}(\text{R})_2$, (R = organic group), or strongly basic quaternary ammonium groups, $-\text{N}^+(\text{R})_3\text{OH}^-$, in which OH^- ion is the replaceable ion. Strongly acidic ($-\text{SO}_3\text{H}$) and strongly basic ($-\text{N}^+(\text{R})_3\text{OH}^-$) ion exchange resins are effective over a wide range of pH and so these are analytically more useful than the weakly acidic and weakly basic types.

Examples (2.51)

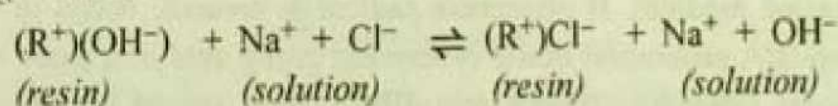
- (i) Strongly acidic cation exchange resins:
Dowex - 50, Amberlite 1R – 120.
- (ii) Strongly basic anion exchange resins:
Dowex-1, Amberlite 1R – 400.

The ion exchange actions maybe represented according to equilibria of the following types:

Cation exchange action:



Anion exchange action:



Thus, when an aqueous solution of a neutral salt such as NaCl is passed through a column of a cation exchange resin in H^+ form, an equivalent amount of acid (HCl) is released. Similarly when such a solution is passed through a column of an anion exchange resin in OH^- form, an equivalent amount of alkali (NaOH) is released. If the anion exchange resin is in nitrate (NO_3^-) form, then an equivalent amount of NaNO_3 is produced on passing a solution of NaCl through it.

The ion-exchange resins, when dry, have shining sand like appearance. When brought into contact with water, the resins take up water molecules by hydration and an increase in volume (*swelling*) takes place. The degree of such swelling decreases with increase of cross linking in the structural net work of the resin. Adsorption of ions by an ion-exchange resin depends upon the charge of the ion. Ions of higher charge are adsorbed more strongly than the ions of lower charge ($\text{Al}^{3+} > \text{Ca}^{2+} > \text{Na}^+$). For ions of same charge type, the extent of adsorption decreases with increase of solvated ionic volumes. Ions of smaller size have greater solvated ionic volumes, consequently they are less strongly adsorbed than the ions of larger size. Among the alkali metal cations, the order of increasing adsorption is : $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$. Due to *lanthanide contraction*, the heavier trivalent lanthanide ions (Ln^{3+}) have smaller size

than the lighter ones. So the heavier Ln^{3+} ions have larger hydrated ionic volumes than the lighter members. Thus, when a solution containing a mixture of such ions is passed through a cation exchange resin column in H^+ form, the heavier ones are weakly held, whereas, the lighter ones are strongly held by the resin. When the column containing the adsorbed lanthanide ions are washed with a suitable liquid containing a complexing ligand that forms water soluble complexes with the adsorbed metal ions (*elution*), the heavier lanthanide ions come out first leaving the lighter ones behind. This forms the basis of separation of lanthanide (Ln^{3+}) ions by ion-exchange method.

The degree of adsorption of ions by ion-exchange resins is strongly influenced by the valency of the ions and also by the dilution of the solution. In general, to exchange a higher valent ion on the exchanger for one of lower valency in the solution, exchange will be favoured on increasing the concentration of the solution. On the other hand, if the lower valent ion is on the exchanger and the higher valent ion is in the solution, exchange will be favoured at higher dilution of the solution.

Separation of metal ions into analytical groups is often hindered due to the presence such anions as PO_4^{3-} , AsO_4^{3-} , CrO_4^{2-} , F^- , BO_3^{3-} , SiO_3^{2-} etc. called *interfering anions*. Removal of F^- , BO_3^{3-} , SiO_3^{2-} are relatively easy. Transformation of AsO_4^{3-} to AsO_3^{3-} and CrO_4^{2-} to Cr^{3+} by reduction, render these anions harmless. $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, SCN^- also interfere by forming intensely coloured solutions and or precipitates. These anions may be decomposed by hot conc. H_2SO_4 (**CAUTION**) (Cf. Sects. 5.8, 5.16, 5.17).

Except NH_4^+ and alkali metal salts, phosphates of most metal ions are sparingly soluble in neutral and alkaline medium. If phosphate radical is present, it has to be separated before entering into Group-IIIa separation in the systematic group analysis, since the reaction medium becomes ammoniacal (alkaline) from Group-IIIa. There are of course several methods of *phosphate separation* involving precipitation of least soluble phosphate salts, viz., ferric chloride method, lead acetate method, stannous chloride method, zirconyl nitrate method etc. All these methods require careful control of pH of the solution. Moreover, all these methods involve one additional step for removal of the excess added cations eg, Fe^{3+} , Pb^{2+} , Sn^{2+} , ZrO^{2+} etc. Ion-exchange method may be conveniently applied for removal of the phosphate ion from the test solution. This requires a strongly acidic cation exchange resin column (Fig. 2.9) in H^+ form. When an acidic (preferably dil. HNO_3) test solution containing several cations and anions including the interfering anions such as phosphate is allowed to pass through the cation exchange resin column in H^+ form, the cations are held up by the resin with release of equivalent amounts of H^+ ions. The anions and neutral species (e.g. H_3PO_4) pass out of the column. Anions in the effluent combine with the released H^+ ion to form the corresponding acids. This effluent solution may also be tested for the anions, except for the one, that is the anion of the acid used to transform the resin into the H^+ form. After washing the column with water to remove any residual anion, the adsorbed cations are eluted from the column by passing dilute ($\sim 2M$) HCl solution. All the metallic ions of the sample solution will now exist as their chloride salts in the effluent solution and may be detected by individual or systematic tests.

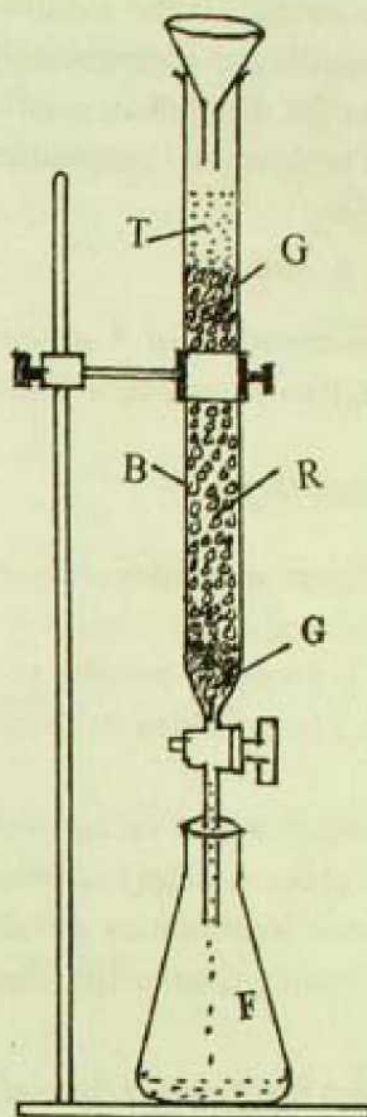


Fig. 2.9. Ion-exchange separation. B = burette (10 ml.) packed with ion exchange resin (R), G = glass wool plug, T = test solution, F = receiver flask (25-50 ml.)

(c) Separation by Solvent Extraction

In qualitative identification of inorganic materials, use is often made of the greater solubility of a particular substance in some solvents than in the others. Suppose a substance, a molecule or an ion or an ion pair, is soluble in two immiscible solvents, producing two different colours, and solubilities of the substance in the two solvents are different. Then, if the solute is shaken with a mixture of these two solvents and the system is allowed to attain equilibrium, the solute will tend to concentrate more in the solvent in which it is more soluble. Such a phenomenon is called *distribution* or *partitioning* of the solute between two immiscible solvents, and it is governed by distribution or partition law, popularly known as *Nernst distribution law*. The law states that, "when a solute distributes between two immiscible and mutually non-interacting solvents and the solute does not react with either of the two solvents, nor the solute undergoes any association, or, dissociation in either of the solvents, then a state of equilibrium is established between the solutions of the solute in the two solvents, such that the ratio of the activities of the solute in the two solvents is a constant, called *partition coefficient* or *distribution coefficient*, which is constant at a given temperature and its magnitude is

independent of the amount of the solute". If the solutions of the solute in both the phases are dilute, then the ratio of the equilibrium concentrations of the solute in the two solvents is also a constant, that is close to the distribution coefficient.

Suppose a solute A distributes between two immiscible solvents say, water and an organic solvent according to the equilibrium,



and $[A]_w$ and $[A]_o$ be the concentrations of A in the aqueous phase and in the organic phase respectively at equilibrium, then according to the distribution law,

$$\frac{[A]_o}{[A]_w} = \text{Constant } (K_d)$$

where, K_d is the partition coefficient or distribution coefficient of A between the two phases. Now, if at equilibrium, the concentration of the solute A is much greater in the organic solvent than that in water ($[A]_o \gg [A]_w$), it may be possible to concentrate the solute A in a small volume of the organic phase from a large volume of the aqueous phase. This is advantageous in two respects:

- (i) In separating A from substances that do not distribute similarly,
- (ii) If the extracted organic phase is deeply coloured, or, fluorescent, then the extract may be useful for qualitative identification and also for quantitative estimation of the solute A by spectrophotometric, fluorimetric, flame photometric, X-ray fluorescence and other methods.

This simple form of the partition law, however, is rarely applied in actual analytical works, since the constituents extracted are often present in more than one forms in the aqueous phase and some times in more than one species even in the organic phase. Under this condition the ratio of the sum of the concentrations of the element in all its forms in the two phases, called the *extraction coefficient* (E), is the one that is more important and useful than the simple distribution ratio (K_d). Extraction coefficient (E_A) of a solute A may be defined as,

$$E_A = \frac{\sum[A]_o}{\sum[A]_w}$$

where, $\sum[A]_o$ = sum of the concentrations of all forms of A in the organic phase and $\sum[A]_w$ is the sum of the concentrations of all forms of A in the aqueous phase.

The major inorganic extraction systems are of four different types:

- (i) *Systems involving simple inorganic species in both aqueous and organic phases:*
Covalent species such as I_2 , Br_2 , $AsCl_3$, SnI_4 , Hg metal (also OsO_4 , RuO_4) etc. dissolve more easily in organic solvents than in water. Non-oxygen organic solvents, such as, CCl_4 , $CHCl_3$, C_6H_6 are better solvents than oxygen containing solvents viz, ether, ketone, esters etc., for extracting these materials from aqueous phase.

(ii) *Extraction of unsolvated association compounds formed with organic reagents:*

Large cations and large anions are only very poorly solvated by water and their solubility in water is very low. Such substances containing organic groups are frequently more or less soluble in organic solvents.

Examples (2.52)

$[\text{Ph}_4\text{As}^+](\text{MnO}_4^-)$: Tetraphenylarsonium permanganate

$[\text{Ph}_4\text{As}^+]_2(\text{CrO}_4^{2-})$: Bis-tetraphenylarsonium chromate

$[\text{Ph}_3\text{MeAs}^+]_2[\text{Co}^{\text{II}}(\text{SCN})_4^{2-}]$: Bis-triphenylmethylarsonium tetrathiocyanatocobaltate

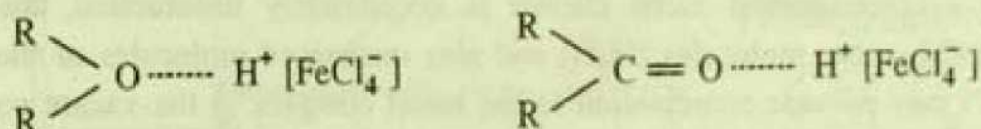
$[\text{R}_4\text{N}^+][\text{UO}_2(\text{ox})_3^-]$: Tetraalkylammonium uranyloxinate

$\text{K}^+[\text{Ph}_4\text{B}^-]$: Potassium tetraphenylboron

Singly charged cations and anions eg. $[\text{Ph}_4\text{As}^+][\text{MnO}_4^-]$ are more easily extracted than multiple charged ions, e.g. $[\text{Ph}_4\text{As}^+]_2(\text{CrO}_4^{2-})$, $[\text{Ph}_4\text{As}^+]_2(\text{MoO}_4^{2-})$ etc. in organic solvents such as CHCl_3 .

(iii) *Inorganic substances forming complexes with the organic solvents:*

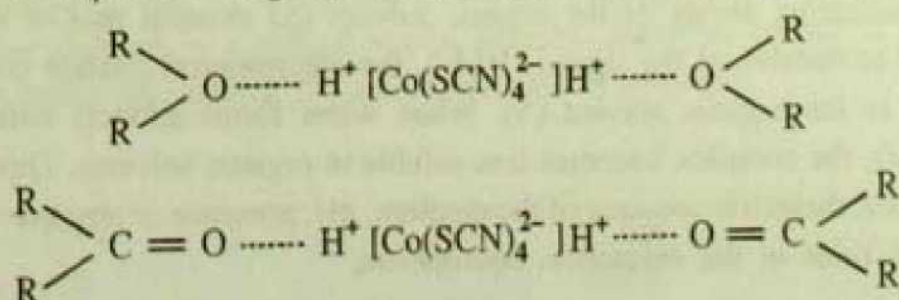
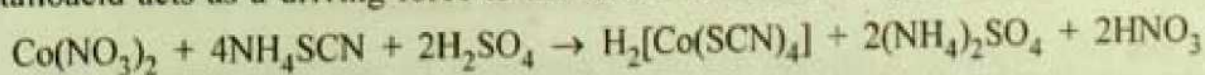
When the inorganic species exist as a complex acids, such as, $\text{H}^+[\text{Fe}^{\text{III}}\text{Cl}_4^-]$, $(\text{H}^+)_2[\text{Co}(\text{SCN})_4^{2-}]$, etc. they become soluble in organic solvents(S) having strongly electronegative atoms, O, N, F etc., due to H-bond formation of the types, $\text{S} \cdots \text{H}^+[\text{FeCl}_4^-]$ etc.,



This is the reason for high solubility of Fe^{III} and other trivalent metal halides in ether, ketone and ester solvents.

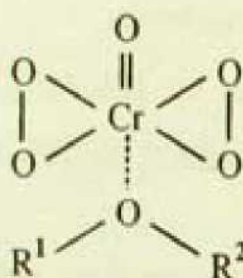
Example (2.53)

(1) Co^{II} salts on treatment with NH_4SCN give a blue coloured complex salt, $(\text{NH}_4)_2[\text{Co}(\text{SCN})_4]$. If the test is carried out in dilute (2M) H_2SO_4 medium, the blue coloured free acid, $\text{H}_2[\text{Co}(\text{SCN})_4]$ is produced, which is much more soluble in ether or amyl alcohol than is the ammonium salt, because, H-bond formation of the solvents with the complex metalloacid acts as a driving force to the extraction of the complex into the organic solvents:



The thiocyanate test for Co^{II} is thus more sensitive in strongly acidic medium.

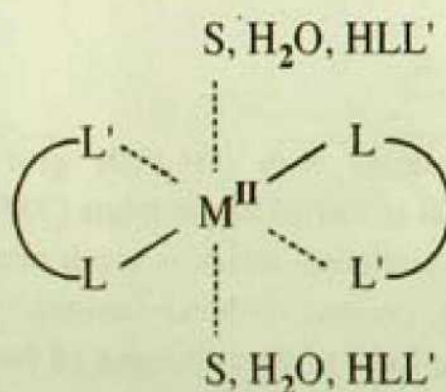
(2) When an acid solution of chromate (CrO_4^{2-}) or dichromate ($\text{Cr}_2\text{O}_7^{2-}$) is treated with H_2O_2 , an intense blue colouration is produced due to the formation of the so called *perchromic acid*, CrO_5 . The blue color is very unstable as perchromic acid soon decomposes yielding oxygen and green solution of chromic salt. However, the blue solution may be stabilized to some extent by extracting it into organic solvents, such as diethyl ether, amyl alcohol, amyl acetate etc. These oxygen containing solvents probably coordinates CrO_5 in which Cr(VI) is coordinately unsaturated:



($\text{R}^1 = \text{alkyl}$, $\text{R}^2 = \text{H, alkyl}$)

(iv) *Extraction of uncharged metal chelates into organic phase:*

When a electroneutral metal chelate is coordinately unsaturated, the organic solvent molecules (S), water molecules (H_2O) and also uncharged molecules of the chelating ligand (say HLL') may provide coordination to the metal complex at the vacant coordination site(s) around the metal atom in the complex:



If the coordinating ability of the organic solvent (S) exceeds that of water molecules or the uncharged molecules of the ligand (HLL'), the electroneutral chelate complex $[\text{M}(\text{L-L}')_2]^0$ is extractable in the organic solvent (S). When water forms adducts with the complex, eg, $[\text{M}(\text{LL}')_2] \cdot x\text{H}_2\text{O}$, the complex becomes less soluble in organic solvents. Dipole moment, of the solvent molecule, dielectric constant of the medium, pH , presence or absence of auxiliary ligands play important roles in the extraction equilibrium.

(d) Electrography

Electrographic methods of simultaneous separation and identification are very useful in qualitative inorganic analysis. Electrography is based on anodic dissolution of the test materials, usually metals, alloys, ores and minerals. The test sample is made the anode and an aluminium block is made the cathode of an electrolytic cell, in which a filter paper moistened with the appropriate reagent solution along with an indifferent electrolyte such as potassium chloride solution, placed between the two electrodes, serves as the electrolyte. When a proper D.C voltage is applied between the two electrodes, migration of cations from the anode material through the reagent paper toward the cathode plate takes place and a print is developed on the reagent paper in such a manner that it is even possible to locate the exact position of the metal ion transferred from the surface of the test sample.

A simplified circuit diagram for fabrication of an apparatus for electrographic separation and identification is shown in Fig. 2.10. An aluminium block (Al) is made the negative pole. A layer of filter paper strips soaked in potassium chloride solution is placed on the aluminium block and upon that, is placed another filter paper strip impregnated with the reagent solution. The test sample (S) is now placed on the reagent paper, and drops of water, acid /alkali/buffer solution etc., auxiliary reagent if any, as required for a particular test are added on the reagent paper, which also serves as the electrolyte. A copper plate (Cu), with a copper rod soldered to it, is placed upon the layers of the filter papers. The Cu plate serves as the positive pole. A 1-5 volt dry cell (E) maybe used as the source of current, which may be controlled by putting a rheostat (R) in the circuit.

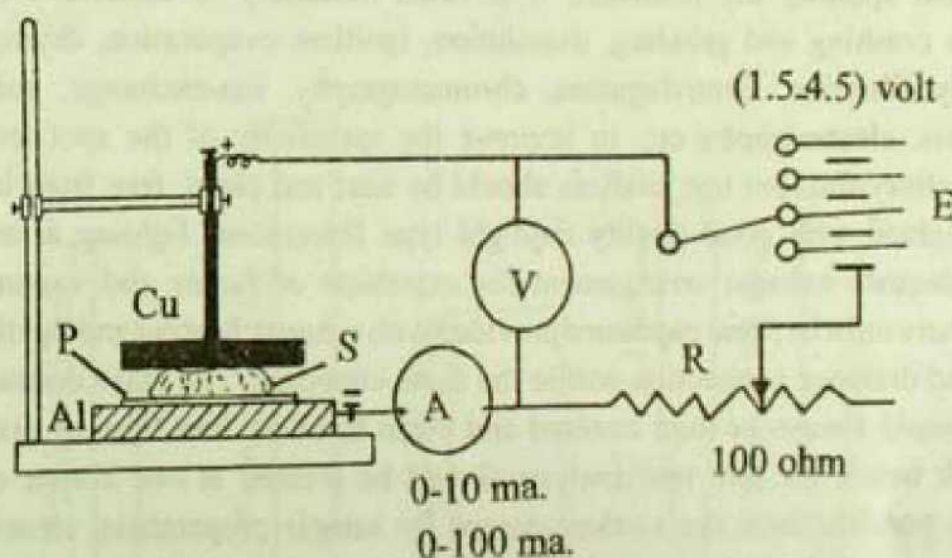


Fig. 2.10. Circuit diagram of electrographic apparatus. Al = aluminium plate, S = test sample, P = reagent paper, A = ammeter, V = voltmeter, R = rheostat, E = D.C. source, Cu = copper plate.

The two electrodes may be connected to the cell through a voltmeter (V) and an ammeter (A). A particular element or a radical maybe detected from the colour of the spot produced on the reagent paper on passing the current for a few minutes.



CHAPTER - 3

Equipment, Techniques and Methodologies

3.1 Introduction

The techniques and methodologies for identification of chemical elements, ions and radicals by sensitive and selective tests based on the chemical reactions involving these materials using a drop or two of the test solution containing them and reagent solution, are given the generic name "*Spot test analysis*". The various ways these tests are conducted have been summarized in Chapter-1 (p. 7). The essential requirements for most successful application of spot tests are the following :

- (i) A sound knowledge of the chemical basis of the reactions involved in every step of the procedure is essential for clear understanding and intelligent execution of the tests.
- (ii) Experimental conditions necessary for a test are to be strictly observed.
- (iii) Laboratory and the equipment are to be scrupulously clean.
- (iv) Purest (AR or GR grade) reagents should be used.
- (v) Blank tests or control experiments are to be carried out to ensure confirmed identification and reproducibility avoiding contamination.

Apart from spotting the reactants, it is often necessary to undertake such preliminary operations as crushing and grinding, dissolution, ignition, evaporation, drying, concentration, separation by filtration, centrifugation, chromatography, ion-exchange, solvent extraction, electrophoresis, electrography etc. to improve the specificity of the spot test analysis.

The laboratory for spot test analysis should be neat and clean, free from laboratory fumes, adequately lighted with good quality daylight type fluorescent lighting arrangements. There should be adequate exhaust arrangement for expulsion of fumes and vapours etc. from the laboratory. There must be *fume cupboard* provided with exhaust, heating and lighting arrangements, water taps and drainage connection within the fume cupboard. The main drainage system of the laboratory should always be kept covered and clean to allow free flow of drainage water.

The work bench for spot test analysis should be located at one corner of the laboratory as remote as possible from the sections meant for sample preparation, cleaning and washing glass apparatus and general macro-chemical operations. The entire unit of spot test analysis should be set up inside a glass chamber/cubical fitted with sliding doors, exhaust, excellent lighting, provided with basin, water taps and drainage connection. The spot test reagents should be kept inside this chamber, other common reagents are to be kept in a nearby place, arranged systematically on racks.

A spot test laboratory should be equipped with variety of chemicals : acids, bases, salts, organic reagents, organic solvents, special reagents etc. as required. For running control experiments, dilute solutions of various metal salts with different anion radicals are to be kept ready. Lists of common and special reagents required in qualitative inorganic analysis are given in Appendix-B1-B10.

3.2 Semi-micro Apparatus

The techniques of semi-micro analysis are not very much different from those used in macro-analysis. The size/volume of the test sample in semi-micro analysis is, however, much smaller, eg. ~ 0.1 g/ ~ 1 ml. Obviously the apparatus are of reduced size. Consequently, manipulations are also easier in semi-micro analysis. Less time and much less reagents/chemicals are required for semi-micro tests. Extreme care, however, should be taken to keep the apparatus and working bench scrupulously clean and reagent racks meticulously arranged.

(a) Test tubes, Boiling tubes, Centrifuge tubes

The size of test tubes used for semi-micro analysis are small (Fig. 3.1). Two types of test tubes (a) $7.5\text{ cm} \times 1\text{ cm}$ ($\sim 4\text{ ml}$) and (b) $10\text{ cm} \times 1.2\text{ cm}$ ($\sim 8\text{ ml}$), may be used for carrying out reactions not requiring boiling. Semi-micro boiling tubes of size $6\text{ cm} \times 2.5\text{ cm}$ ($\sim 6\text{ ml}$) (Fig. 3.1c) are used for rapid concentration or digestion operations requiring boiling of the test solutions. Semi-micro centrifuge tubes (Fig. 3.1d) of length $\sim 7.5\text{ cm}$ are used for separating a precipitate from a solution. These are test tubes with narrowed bottom. Graduated centrifuge tubes (Fig. 3.1e) are also available. Average diameter of a semi-micro centrifuge tube should be ~ 1 to 1.2 cm and its mouth should be ~ 1.3 to 1.5 cm wide. Less than half of its height should be filled for centrifugation. Another centrifuge tube of identical size and weight filled up to the same height with water, should be placed on the side opposite to the one containing test sample for balance. All these tubes should be made of good quality glass (Borosil/Pyrex).

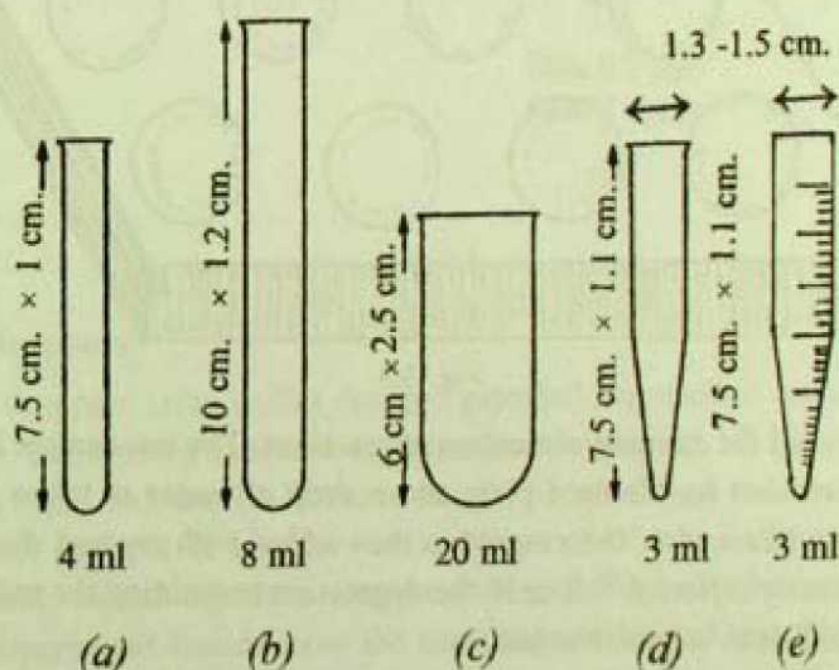


Fig. 3.1

Test tubes, boiling tubes etc. may be held by test tube holders (Fig. 3.2a), which may be of various types, made of light metals with wooden/amber handles. Nylon brushes of various types (Fig. 3.2 b,c) are available for cleaning the test tubes, centrifuge tubes etc.

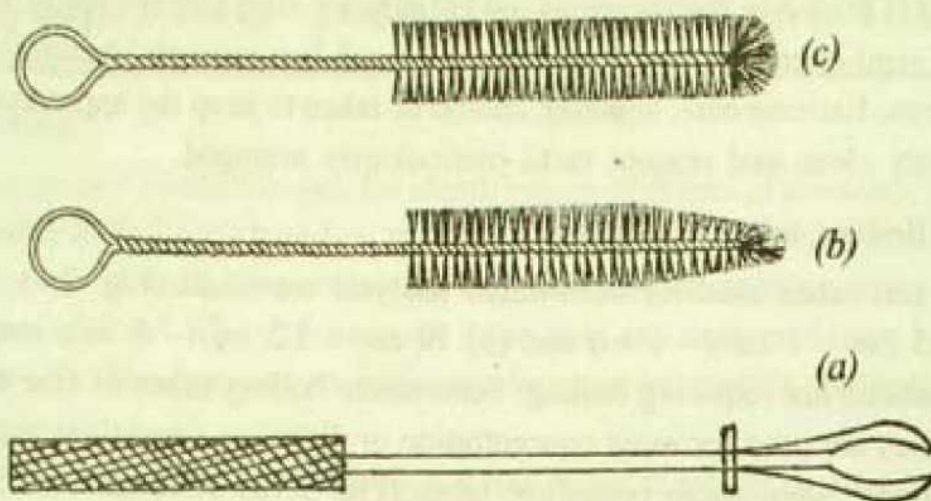


Fig. 3.2

(b) Spot plates

Spot plates are good quality white or black glazed porcelain blocks (Fig. 3.3) of average dimensions : $(8-10) \text{ cm} \times (6-4) \text{ cm} \times (1.5-2) \text{ cm}$ with 3 to 4 pairs of depressions of roughly 1 to 1.5 cm in diameter and $\sim 0.5 \text{ cm}$ in depth, of capacity $\sim 0.5 \text{ ml}$ on top.

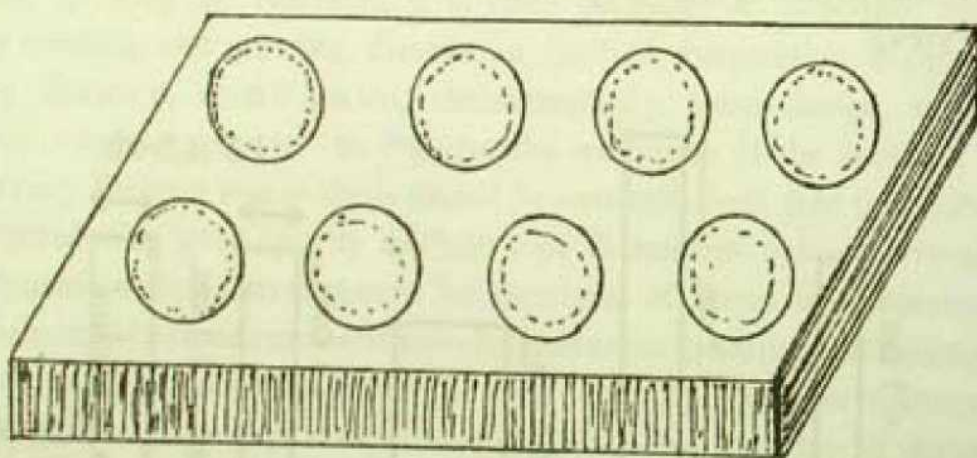


Fig. 3.3

Spot plates are used for carrying out coloured reactions. The test sample itself or its solution is placed on a depression on the spot plate and a drop of water is taken on the depression adjacent to it for the blank test. The reagent is then added with reagent droppers on both the depressions. A distinctly different colour in the depression containing the test sample from that of the blank run indicates a positive test.

White porcelain background of the spot plate enables detection of even very minute colour changes. Black spot plates are useful for light coloured or white coloured materials. Transparent glass spot plates may also be used by placing it on a glossy paper of suitable contrasting colour. Test solution and the reagent drops should be properly mixed in the depressions on the spot plate using a glass stirring rod or a stout platinum wire.

(c) Stirring rods

Stirring is very often required in semi-micro tests for uniform mixing of the reagents with the test sample/solution. Small glass rods of 10-12 cm length and 2 mm in diameter are most convenient for stirring of small volume of solutions (Fig. 3.4a). The end of the rod may be rounded by heating to fusion on non-luminous Bunsen flame and then rolling the soften rod on an asbestos board. For convenient operation, a handle may be formed at one end of the rod by bending it through an angle of $\sim 45^\circ$ to 135° after heating the rod to fusion on the flame (Fig. 3.4b). For uniform mixing of the test sample with the reagent on a spot plate, a glass rod may be drawn into a thin needle and a small glass bead may be formed at its end (Fig. 3.4c).

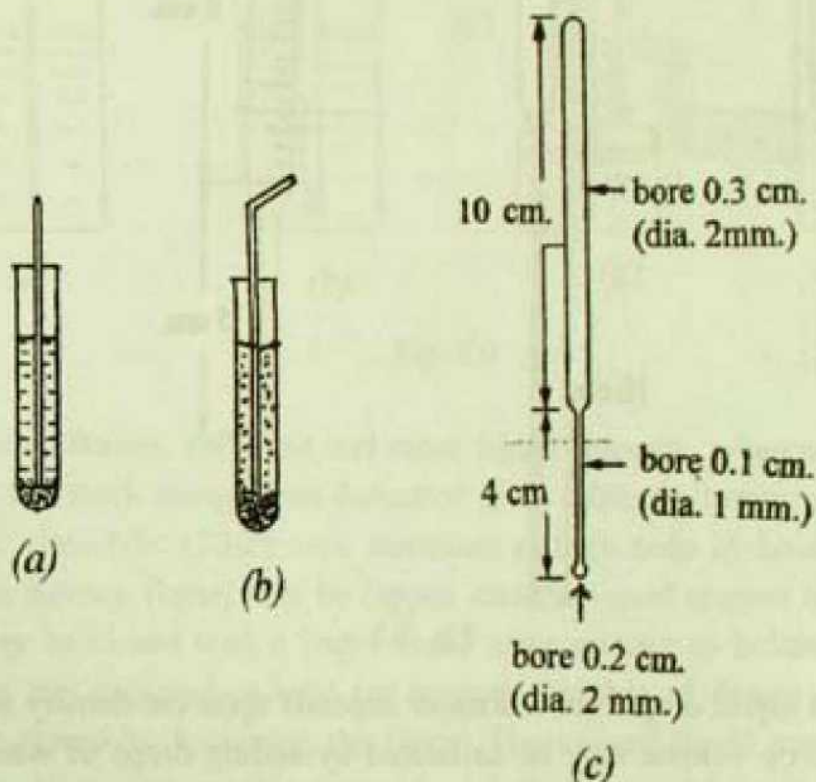


Fig. 3.4

(d) Semi-micro droppers

Two types of droppers (also called dropper pipettes) are used in semi-micro operations. Droppers used for transferring reagents from reagent bottles of 50-100 ml capacity, called *reagent droppers* (Fig. 3.5a), are 10-12 cm in length, of which ~ 4 to 5 cm is a capillary tube at the dropping end. Dropper of length ~ 15 to 20 cm of which ~ 10 cm is a capillary tube at the dropping end, called *capillary droppers* (Fig. 3.5b), may be used for transferring centrifugate and supernatant liquids from the centrifuge tubes and test tubes. These droppers may also be used for adding test solutions or reagents to the drop reaction papers or on the spot plate. For quantitative transfer of definite volumes of liquid, *graduated dropper pipettes* (Fig. 3.5c) may be used. *Transfer capillaries* (Fig. 3.5d) drawn from wider glass tubes or test tubes are useful for transferring minute volumes of liquids for spot reactions.

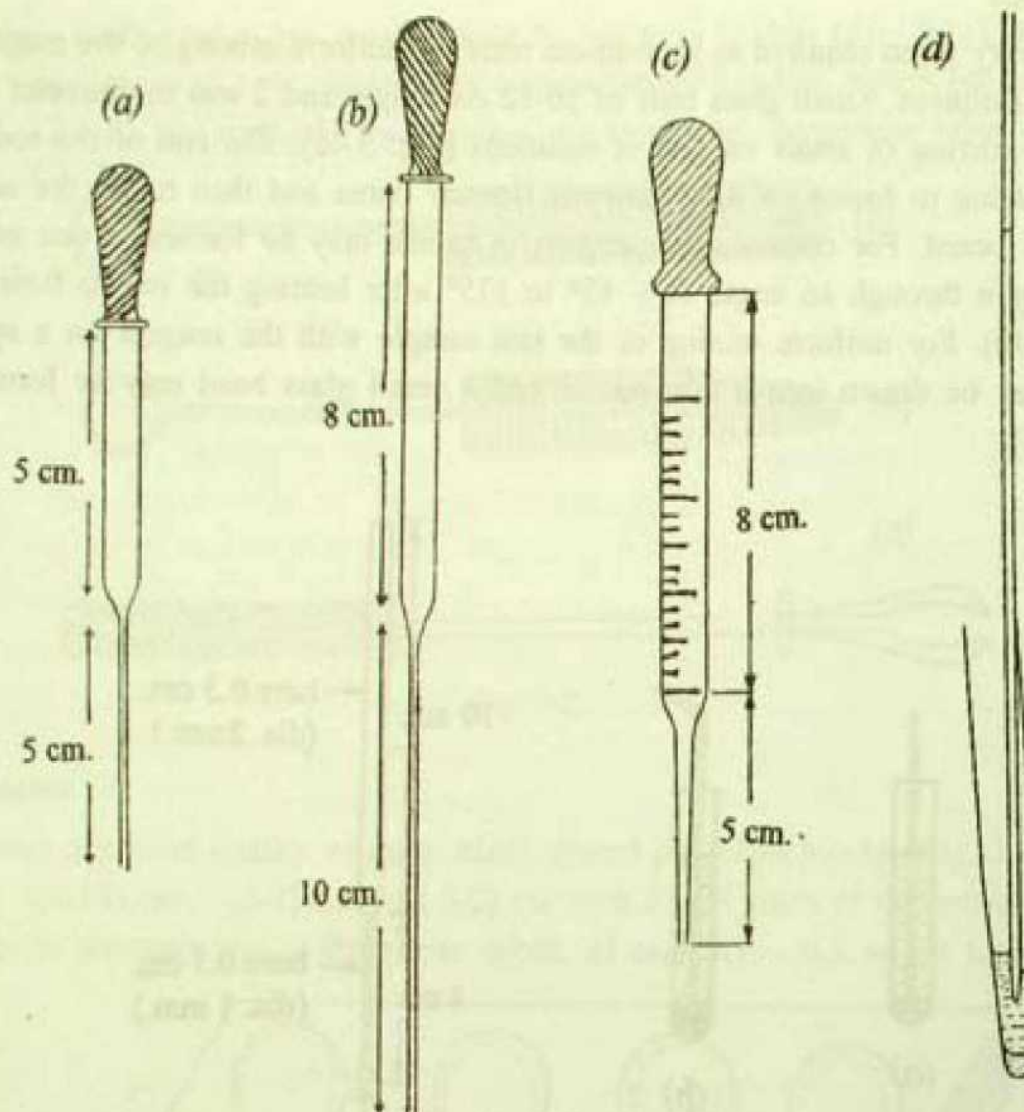


Fig. 3.5

The volume of a liquid drop from a dropper depends upon the density and surface tension of the liquid. The drop volume may be calibrated by adding drops of water from a dropper into an empty 5 ml measuring cylinder up to a definite volume, while counting the number of drops. Volume of a drop of water may be obtained by dividing the volume of water with the number of drops. The capillary of the dropper should be such that ~ 30 to 40 drops of water passing through it should make a volume of 1 ml. If a dropper delivers 20 drops per 1 ml of distilled water, it will deliver approximately 20-22 drops of dilute aqueous solutions of acids, bases and salts, 23-24 drops of concentrated hydrochloric acid, 36-37 drops of concentrated nitric acid or concentrated sulfuric acid, ~ 63 drops of acetic acid and 24-25 drops of ammonia solution per 1 ml.

(e) Reagent bottles

Reagent bottles should be well stoppered and clearly labelled. 250 ml reagent bottles are suitable for common reagent solutions. Acid solutions may be stored in clean glass bottles, or, polythene bottles. Alkali solutions should better be kept in polythene bottles. Organic solvents and organic reagents may be stored in the original bottles, preferably in a darkened cabinet, and if necessary, may be kept inside a refrigerator. Liquid reagents for spot test analysis

should be kept either in dropping bottles (Fig. 3.6a) made of glass or polythene, or in pipette bottles (Fig. 3.6b) provided with capillary droppers. Special, costly reagents may be kept in Barnes dropping bottles (Fig. 3.6 c,d). For transferring drops of concentrated acids, alkalis etc. glass stoppered dropping bottles (Fig. 3.6e) are most convenient. Larger volumes of

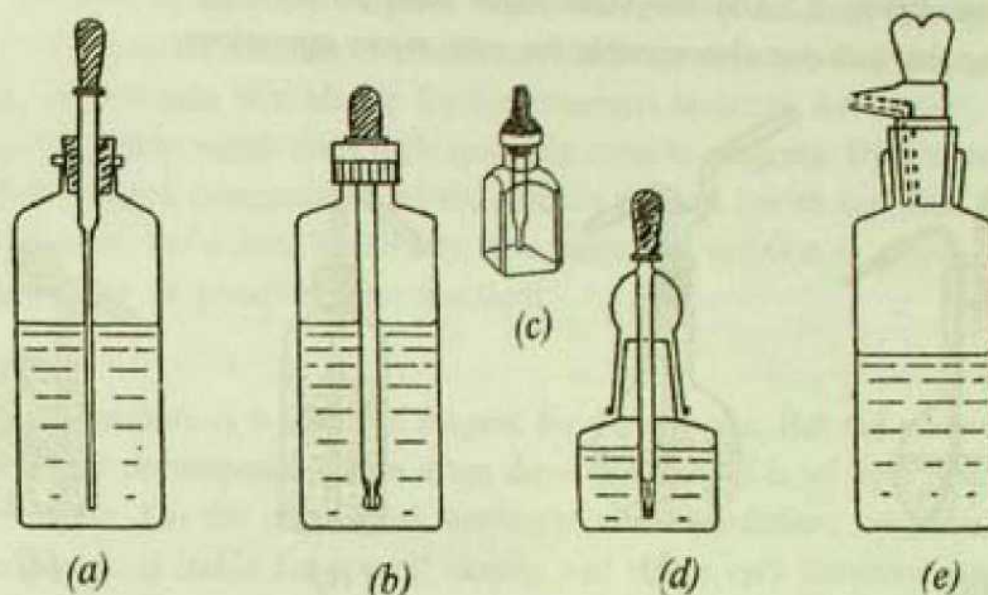


Fig. 3.6

concentrated acids, alkalis, ammonia and other liquid reagents, whenever necessary, may be transferred from the stock using clean dedicated glass tubes or droppers of appropriate sizes. For this purpose, glass tube (20-25 cm), smoothen at both ends by holding for some time in the non-luminous Bunsen flame, may be dipped into the liquid reagent by $\sim 1-2$ cm, and then the upper end may be closed with a finger in the same manner as holding a pipette. The tube is then taken out and required volume (or required number of drops) of the liquid reagent may then be transferred by loosening the finger. The unused liquid may then be returned to the original bottle. Since very small volumes ($\sim 1-2$ drops or $\sim 0.5-1$ ml) of the liquid reagents are used in majority of the spot tests, this method of transferring liquid is not only most convenient, but also economic and less hazardous.

Solid reagents should be kept in wide mouth, small ($\sim 100-150$ ml capacity) well stoppered glass or polythene reagent bottles. Clean horn *spatula* or nickel or nickel plated steel spatula should be used for transferring solid reagents from the bottles.

Note

After using a reagent, the stopper, cork or cover of the reagent bottles should be replaced in its position to avoid any contamination. Under no circumstances a reagent bottle should be kept open.

(f) Wash bottles

In semi-micro qualitative inorganic analysis, washing of the precipitate, dilution of a solution, cleaning of the apparatus etc., with distilled water are very often required. 50-100 ml capacity

reagent bottles, fitted with reagent droppers (Fig. 3.6 a,b) may be a suitable container for distilled water. For washing with larger volumes of water, wash bottles of various types (Fig. 3.7) are available. 250 ml flat bottomed flasks with a jet of 0.5-1.0 mm diameter, fitted at its mouth with a rubber cork or with full ground glass joints, are the most common types of wash bottles. These are mouth operated (Fig. 3.7 a,b). Polythene made wash bottles (Fig. 3.7 c,d) of ~ 100-250 ml capacity, having fine jets are also suitable for semi-micro operations.

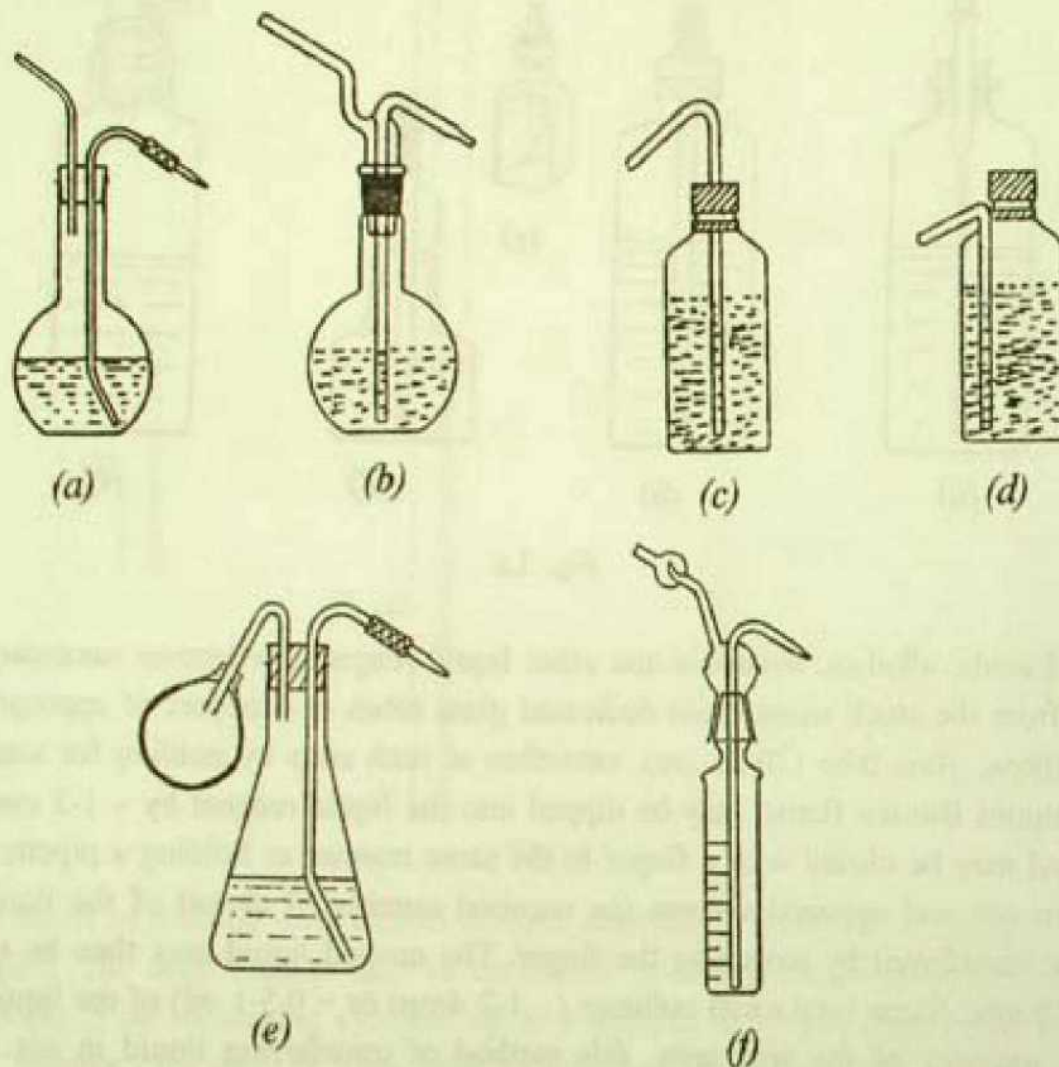


Fig. 3.7

Wash liquid is dispensed from these polythene bottles by squeezing. For washing with hot water, a 100-150 ml capacity conical flask, fitted with a hand operated rubber bulb (Fig. 3.7e) is most convenient. For transferring definite volume of liquid, a small (~ 25 ml) graduated wash bottle (Fig. 3.7f) may be used.

(g) Drop-reaction paper

Strips of Whatman No. 1 filter paper may be used for spot tests. The filter paper sheet may be cut into strips of 5 cm × 2 cm and 2 cm × 2 cm sizes and stored in petri dishes or in wide mouth and stoppered bottles.

Impregnated reagent papers may be prepared by bathing the strips of Whatman No. 1 filter paper in the reagent solutions and then drying in air. Alternatively, the reagent solutions may

be sprayed on the filter paper strips, which are then dried in air. Uniform impregnation and uniform drying are of great significance.

Water soluble alkali metal salts and ammonium salts are not very stable on filter papers. Sparingly soluble salts of other metals serve as better reagents on filter paper reactions. Although it might be expected that insoluble reagents would slow down the reactions rates, but when the filter paper serves as the medium, it transforms the reagents into a fine state of dispersion, so that, a large surface area is available for the reactions to occur. As a result, reactions on filter paper are extremely rapid, even with sparingly soluble reagents. By proper selection of the impregnating reagent, concentration of the reactive reagent ion on the filter paper may be controlled as required for a test. Specificity of a particular reaction is greatly increased by restricting the number of possible other reactions.

Examples (3.1)

(1) Potassium xanthate is a selective reagent for Cu and Mo. But the reagent is not very stable in solution. It decomposes within a ten days. As such, it is of very little value as an impregnating reagent. On the other hand, sparingly soluble cadmium xanthate, impregnated on filter paper strips, is stable for several months and it is a very sensitive reagent for only Cu and Mo.

(2) Use of sparingly soluble metal sulfides as impregnating reagents for detection of other metals as their sulfides on filter paper strips is strictly controlled by solubility product principle (*cf.* Sect 2.2). For a successful test, the solubility product of the sulfide of the metal ion in the test solution should be lower than the solubility product of the reagent metal sulfide. Thus, antimony (III) sulfide impregnated filter paper precipitates only sulfides of silver, copper, bismuth and mercury in presence of lead, cadmium, tin, iron, nickel, cobalt and zinc, as the solubility products (K_{sp}) of the metal sulfides imply (Table 3.1).

Table 3.1 Solubility products (K_{sp}) of some metal sulfides at 25°C

$$(K_{sp})_{MS} = [M^{2+}] [S^{2-}], (K_{sp})_{M_2S} = [M^+]^2 [S^{2-}], (K_{sp})_{M_2S_3} = [M^{2+}]^2 [S^{2-}]^3$$

Ag ₂ S	6×10 ⁻⁵⁰	Sb ₂ S ₃	1.5×10 ⁻⁹³	PbS	2.5×10 ⁻²⁷	NiS	3×10 ⁻¹⁹
CuS	6×10 ⁻³⁶	FeS	6×10 ⁻¹⁸	CdS	8×10 ⁻²⁷	CoS	2×10 ⁻²⁵
HgS	1.6×10 ⁻⁵²	Bi ₂ S ₃	1×10 ⁻⁹⁷	SnS	1×10 ⁻²⁵	ZnS	5×10 ⁻²⁵

(3) Filter paper impregnated with freshly precipitated zinc sulfide precipitates CuS (black) and CdS (yellow). Although a black spot due to CuS is initially visible, however, separation and detection of both metals are possible by adjustment of acidity and capillary separation technique (*cf.* Sect. 2.2, p-57)

(4) Pale yellow (or almost white) coloured potassium zinc ferrocyanide, K₂Zn₃[Fe(CN)₆]₂, impregnated on a filter paper, serves as a source of ferrocyanide Fe(CN)₆⁴⁻ ion and provides highly sensitive Prussian blue test for iron (III).

3.3 Reagents

Reagents used in qualitative inorganic analysis may be divided into the following groups for convenience of operations.

(1) Workbench reagents

Reagent solutions which are frequently required in carrying out most of the reactions, should be kept on each individual working desk, arranged in solid wooden stand. A list of such reagents are given in Table 3.2 (Sect. 3.7) along with the types of reagent bottles in which these reagents are to be kept.

(2) Liquid reagents

Reagent solutions which are less frequently used, are to be kept in 50-100 ml dropping bottles. A list of such reagents is provided in Appendix-B1-B4, B6-B9. These reagents are to be kept in a common place.

(3) Solid reagents

Solid reagents (Appendix-B5) should also be kept in a common place in wide mouth stoppered bottles provided with small spatulas.

(4) Special reagents

Special reagents should be kept inside a glass housing, provided with sliding doors. Since most of the special reagents are highly expensive, these reagents should be kept in small dropping bottles (30-50 ml), provided with reagent droppers. A list of such reagents is provided in Appendix-B10.

Reagents should be arranged in the reagent rack in the alphabetical order of their trivial names and the reagent bottles should be clearly labelled and serially numbered. A list of the reagents according to their trivial names in the alphabetical order should be displayed near the reagent rack for easy access.

Note

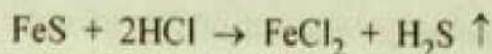
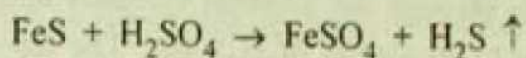
In using the reagents from the common rack, great care should be taken to avoid contact of the reagent dropper or spatula with the test sample/solution. Since the semi-micro tests are highly sensitive, slightest contamination of the reagent may produce wrong observation. If any such contact takes place by an accident, the dropper or the spatula should be thoroughly washed with distilled water and wiped with a clean cloth or a tissue paper. The capillary end of the reagent dropper should never be dipped into any other solution.

(5) Gaseous reagents

Gaseous reagents such as hydrogen sulfide (H_2S), sulfur dioxide (SO_2) and chlorine (Cl_2) are often generated in the laboratory for preparation liquid reagents, viz, H_2S -water, SO_2 -water, Cl_2 -water. These gases are generated in specially designed apparatus, in *fume cupboard* having proper exhaust arrangement. The apparatus should be dismantled and the exhausted chemicals should be disposed of at a place far remote from the activity area when the laboratory session is off.

(a) Hydrogen sulfide (H_2S) and H_2S -water

Hydrogen sulfide may be generated in the laboratory at ordinary temperature by the action of dilute (6M) hydrochloric acid or sulfuric acid on ferrous sulfide (FeS) in Kipp's apparatus (Fig. 3.8a), kept inside a *Fume Chamber*.



The gas emerging from the Kipp's apparatus is contaminated with acid vapours and ferrous salts. It should be washed free from these impurities by passing through water in a bubbler (Fig. 3.8b). The bubbler outlet tube should be fitted with a small piece of rubber tubing to

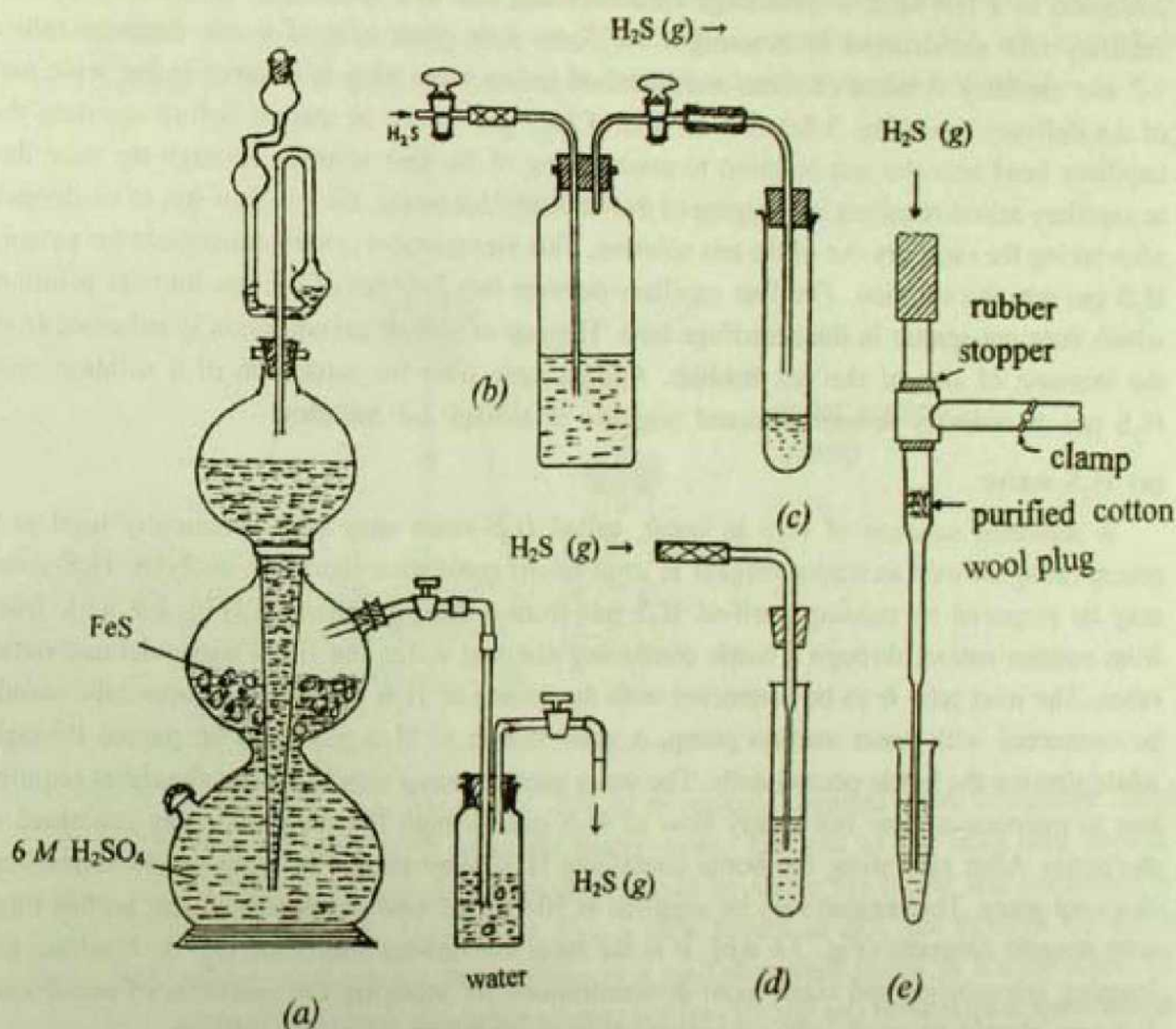


Fig. 3.8

which is connected a clean thick walled glass delivery tube drawn into a capillary and fitted with a cork. A slow stream of H_2S gas may be passed through the solution for about 20-30 seconds in order to expel air. Then the cork is to be pushed into position (Fig. 3.8 c,d) and

the passage of H_2S gas continued with occasional shaking until very few gas bubbles pass through bubbler solution. It should be kept in mind that in precipitation by H_2S gas, only the dissolved part of the gas reacts with the metal ions in solution. So the stream of the gas should be so slow that the bubbles in the bubbler wash bottle can be easily counted. Otherwise, a huge amount of H_2S gas will pass through the solution uselessly and will pollute the air. Very serious poisoning may occur due to inhalation of H_2S gas. The tap of the H_2S gas generator should be closed after taking the delivery tube out of the solution to avoid clogging of the capillary by the precipitate. Increase in the size of the gas bubbles indicates completion of absorption of the gas into the solution.

In semi-micro qualitative inorganic analysis, H_2S gas may be lead into the test solution contained in a test tube or centrifuge tube avoiding loss and spattering, by means of a fine capillary tube constructed by drawing a 10-15 cm long glass tube of 6 mm diameter into a 1-2 mm capillary. A piece of clean and bleached cotton wool plug is inserted in the wide part of the delivery tube (Fig. 3.8e). The stream of H_2S gas has to be started before inserting the capillary head into the test solution to avoid rising of the test solution through the tube due to capillary action resulting in clogging of the capillary. Likewise, the gas flow has to be stopped after taking the capillary out of the test solution. This arrangement is very convenient for passing H_2S gas into the solution. The fine capillary delivers tiny bubbles of the gas into the solution, which does not spatter in the centrifuge tube. The end of sulfide precipitation is indicated from the increase of size of the gas bubbles. Approximate time for saturation of a solution with H_2S gas at ordinary temperature and pressure is around 2-3 minutes.

(a) H_2S -water

A saturated solution of H_2S in water, called H_2S -water may be conveniently used as a precipitating as well as a spot reagent in semi-micro qualitative inorganic analysis. H_2S -water may be prepared by passing purified H_2S gas from a Kipp's apparatus (Fig. 3.8 a,b), freed from contamination, through a bottle containing distilled water and fitted with inlet and outlet tubes. The inlet tube is to be connected with the source of H_2S gas and the outlet tube should be connected with water suction pump. A slow stream of H_2S gas is to be passed through, while shaking the bottle occasionally. The water suction pump should be run slowly as required just to maintain a slow but steady flow of H_2S gas through the distilled water contained in the bottle. After saturation, the bottle containing H_2S -water should be tightly corked and kept in a cool place. The reagent may be supplied in 50-100 ml well stoppered reagent bottles fitted with reagent droppers (Fig. 3.6 a,b). It is the most convenient source of H_2S in teaching and learning laboratories and class room demonstrations for studying the reactions of metal ions. H_2S gas should be used only for quantitative precipitation of metal sulfides.

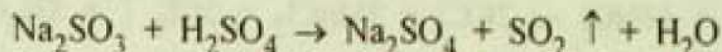
Note

All operations with hydrogen sulfide including its preparation must be conducted inside a **Fume Chamber** having proper exhaust arrangement. All connections should be sealed with parffin wax. **Hydrogen sulfide is deadly poisonous** and its lethal dose is very low, almost

same as that of **hydrogen cyanide (HCN)**. Its unpleasant smell fortunately repel people from breathing it in dangerous amount.

(b) Sulfur dioxide (SO₂) gas and SO₂-water

Sulfur dioxide (SO₂) gas can be generated in the laboratory at ordinary temperature by the action of dilute (8M) sulfuric acid on sodium sulfite.



Make a slurry of around 60-65 g. of anhydrous sodium sulfite and ~50 ml of water in a large filtering flask (1 litre) provided with a delivery tube and fitted with a dropping funnel with the aid of a rubber cork (Fig. 3.9). The end of the dropping funnel should be slightly inside the slurry. Take ~ 125 ml 8M sulfuric acid in the dropping funnel and introduce the acid in small portions at a time, while shaking the flask occasionally. SO₂ gas is produced instantaneously. Wash the gas by passing it through a bubbler containing water.

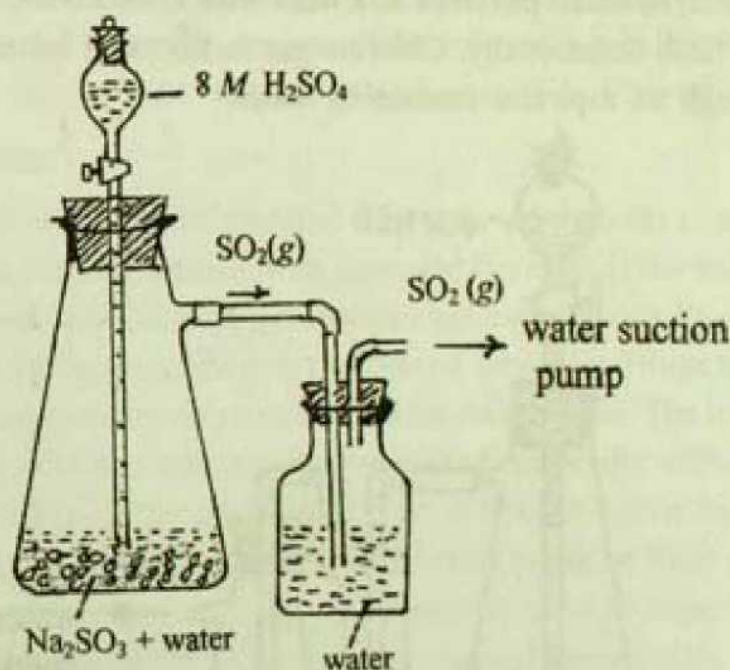


Fig. 3.9

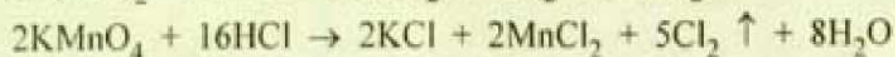
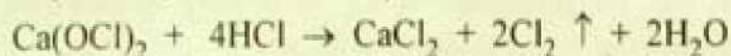
For preparation of SO₂-water, take ~ 200 ml of ice-cold distilled water in another filtering flask (~ 500 ml) provided with inlet and outlet tubes. The end of the inlet tube should be dipped slightly into water and the outlet tube should be above the liquid and connected with water suction pump through a regulator. Pass a slow stream of SO₂ gas through the distilled water until saturation. Preserve the solution in a well stoppered bottle in a cool place. SO₂-water may be supplied in well stoppered reagent bottles (50-100 ml) fitted with reagent droppers (Fig. 3.6 a,b).

Note

The apparatus should be set up in side a *Fume Chamber* and all connections should be sealed with paraffin wax.

(c) Chlorine gas (Cl_2) and Cl_2 -water

Chlorine gas (Cl_2) may be generated in the laboratory at ordinary temperature by the action of dilute (6M) hydrochloric acid on (i) Calcium hypochlorite $\text{Ca}(\text{OCl})_2$ or bleaching powder or (ii) Potassium permanganate (KMnO_4) :



(i) From Calcium Hypochlorite :

Moisten a 1:1 mixture of calcium hypochlorite or bleaching powder and gypsum powder ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) with little water and prepare small lumps of the mixture. Allow the lumps to dry in air. Introduce the lumps (~ 50g) into a large filtering flask (1 litre) having a delivery tube and fitted with a dropping funnel with aid of a rubber cork (Fig. 3.10). Cover the lumps with a little water and dip the end of the dropping funnel into it. Introduce ~ 125 ml of 6 (M) hydrochloric acid, **in small portions at a time with CAUTION**, from the dropping funnel, while shaking the flask occasionally. Chlorine gas is liberated instantaneously. Wash the gas by passing it through an aspirator containing water.

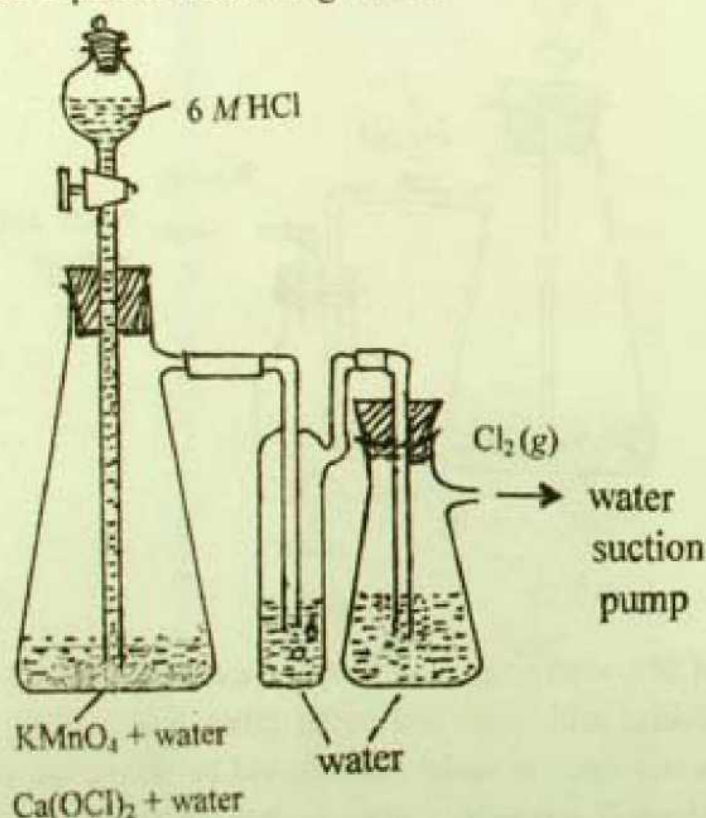


Fig. 3.10

For preparing chlorine-water, pass the purified and washed Cl_2 gas through ~ 200 ml of ice-cold distilled water taken in a filtering flask (~ 500 ml) provided with inlet and outlet tubes. The end of the inlet tube should be dipped into distilled water. The outlet tube should be connected to a water suction pump. A slow stream of Cl_2 gas should be passed through water until saturation. Cl_2 -water solution should be stored in well corked dark coloured bottles in a cool place. It may be supplied in 50-100 ml reagent bottles fitted with reagent droppers (Fig. 3.6 a,b).

(ii) From Potassium Permanganate

Cl_2 gas may also be prepared at ordinary temperature by treating a slurry of ~ 15 g of KMnO_4 with ~ 125 - 130 ml of 6 (M) hydrochloric acid in a same type of apparatus (Fig. 3.10) as described for preparation of the gas from calcium hypochlorite. Cl_2 -water may be prepared, stored and supplied in the same manner as described.

Note

The apparatus for generation of SO_2 and Cl_2 gases should be set up inside a *Fume Chamber* and all connections should be sealed with paraffin wax. The apparatus should be dismantled at a place remote from the activity area when the laboratory session is off.

3.4 Semi-micro Operations

Techniques of cleaning, preparation of the test sample/solution, heating, digestion, evaporation, boiling, distillation etc. will be discussed in this section. Techniques of separation by filtration/centrifugation and special techniques for identifying gaseous reaction products will be discussed separately in the following sections. Principles of separation by chromatography, ion-exchange, solvent extraction have been briefly discussed in Chapter-2.

(a) Cleaning of apparatus

Scrupulous cleanliness is absolutely essential for trustworthy results in semi-micro analysis. All apparatus should be thoroughly cleaned with chromosulfuric acid (chromic acid solution) (*cf.* Appendix-B1) or by brushing with cleaning powders or cleaning solutions. Special types of brushes (Fig. 3.2 b,c) may be used for cleaning the inside of the test tubes, centrifuge tubes and other glass apparatus. Commercial pipe cleaners may also be used for this purpose. The apparatus should then be thoroughly washed with running water and finally washed repeatedly with distilled water.

The washed apparatus should be allowed to drain out water either by holding on stands or by inverting on a beaker having several folds of blotting paper or filter paper at the bottom to absorb water. Small towel, clean cloth etc. may also be used to wipe out water from the larger apparatus. Glass tubes, droppers etc. should be cleaned immediately after use. Droppers should be cleaned by removing the rubber teats and passing distilled water repeatedly through the glass tube. The teats should be cleaned by repeatedly filling with distilled water and squeezing out. Clean apparatus should be covered with dry linen glass cloth or polythene sheet. At the end of the laboratory session, the cleaned apparatus should be kept in covered boxes or in desks, so that these remain clean for future use.

(b) Preparation of test samples/solutions

Solid samples subjected to spot test analysis should be first brought into solution by dissolution in water, acids, caustic alkalies, or by fusion [with anhydrous Na_2CO_3 or potassium hydrogen sulfate, KHSO_4 (the actual reactant is potassium pyrosulfate, $\text{K}_2\text{S}_2\text{O}_7$)] followed by extraction with water. Some times volatilization, extraction with organic solvents, chromatography and ion-exchange separation techniques are also employed for separation and identification of inorganic radicals. Whatever treatment is employed, rapid and complete

reaction for dissolution occurs if the material is in a finely powdered or pulverized state, which provides maximum reactive surface area to the sample for dissolution. Agate mortar or, good quality glass or porcelain mortars with pestles of the same materials (Fig. 3.11) are commonly used for pulverizing the solid samples.

Very hard particles may be broken with steel mortars before final pulverizing in an agate mortar.

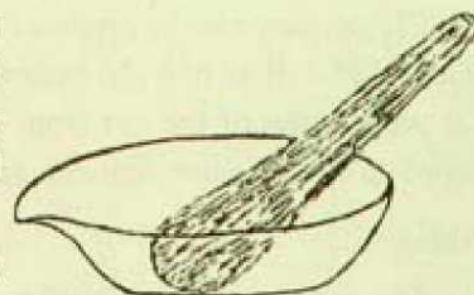
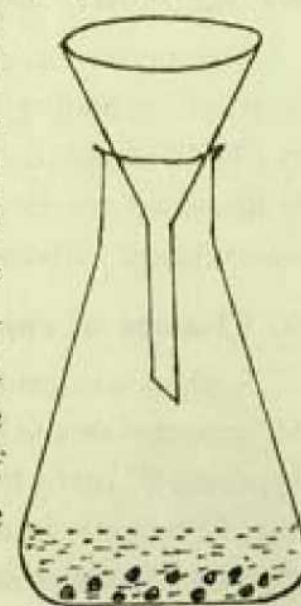


Fig. 3.11

(c) Dissolution

For dissolution of solid samples or for extraction of fused melts or for preparing NaOH or Na_2CO_3 extracts, small amount (~ 0.5 g) of the material may be placed in a small (~ 25 - 50 ml) conical flask along with 5-10 ml of distilled water, acid, alkali etc. as required. The mouth of the conical flask should be covered with a small funnel (Fig. 3.12) to prevent loss due to bumping and spattering. The funnel cover also acts as a condenser to prevent loss of the liquid due to evaporation. The conical flask with its contents should be placed on a wire-gauge or asbestos board as required and heated in the non-luminous flame of the burner. Heating may also be conducted on a hot plate, sand bath, steam bath or hot water bath as required. Digestion with volatile acids (HCl, HNO_3 aqua-regia etc.) or reactions involving liberation of gaseous products such as H_2S , SO_2 , NO_2 , NO , NH_3 etc. should be conducted inside a Fume Cupboard.



test sample + reagent

Fig. 3.12

(d) Heating, Evaporation, Drying, Fusion, Ignition

These operations require moderate to strong heating of the solid sample or the test solution alone or with appropriate reagents. Evaporation is often required for concentrating the solutions, removing solvents etc. Evaporation to dryness is carried out to isolate the dissolved solute in the solid state from a solution. In either case, evaporation requires moderate heating, which may be carried out by gentle heating on an asbestos board or on a hot water bath. Strong direct heating for a longer time in the hottest part of the Bunsen flame (cf. Fig. 6.1) may be required for fusion, which may be carried out on platinum spoon (Fig. 3.13a), in fusion tubes or on mica foils, in special cases on a platinum wire loop.

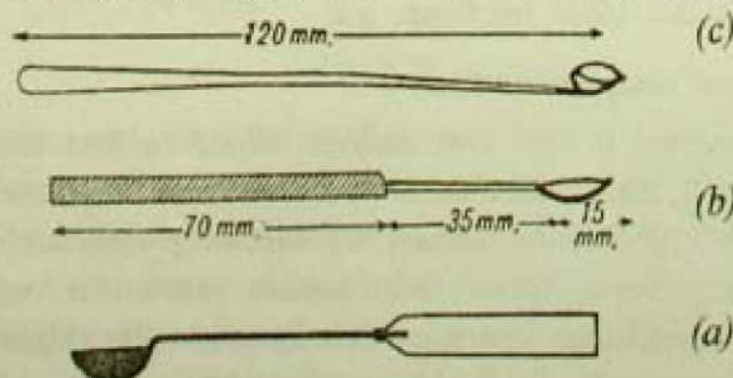


Fig. 3.13

Hot block

Evaporation of solutions may be conveniently carried out in small beakers, porcelain or silica, or platinum or nickel micro crucibles. It is often necessary to carry out the evaporation at low temperature to avoid decomposition of certain compounds. Evaporation at low temperature may be achieved under reduced pressure. An apparatus for evaporation under reduced pressure is shown in (Fig. 3.14a). An aluminium block (A) with 2-3 cavities for housing micro crucibles (C), fitted with a hole for a thermometer (T) is taken. A bell jar (B) with a stop cock is placed

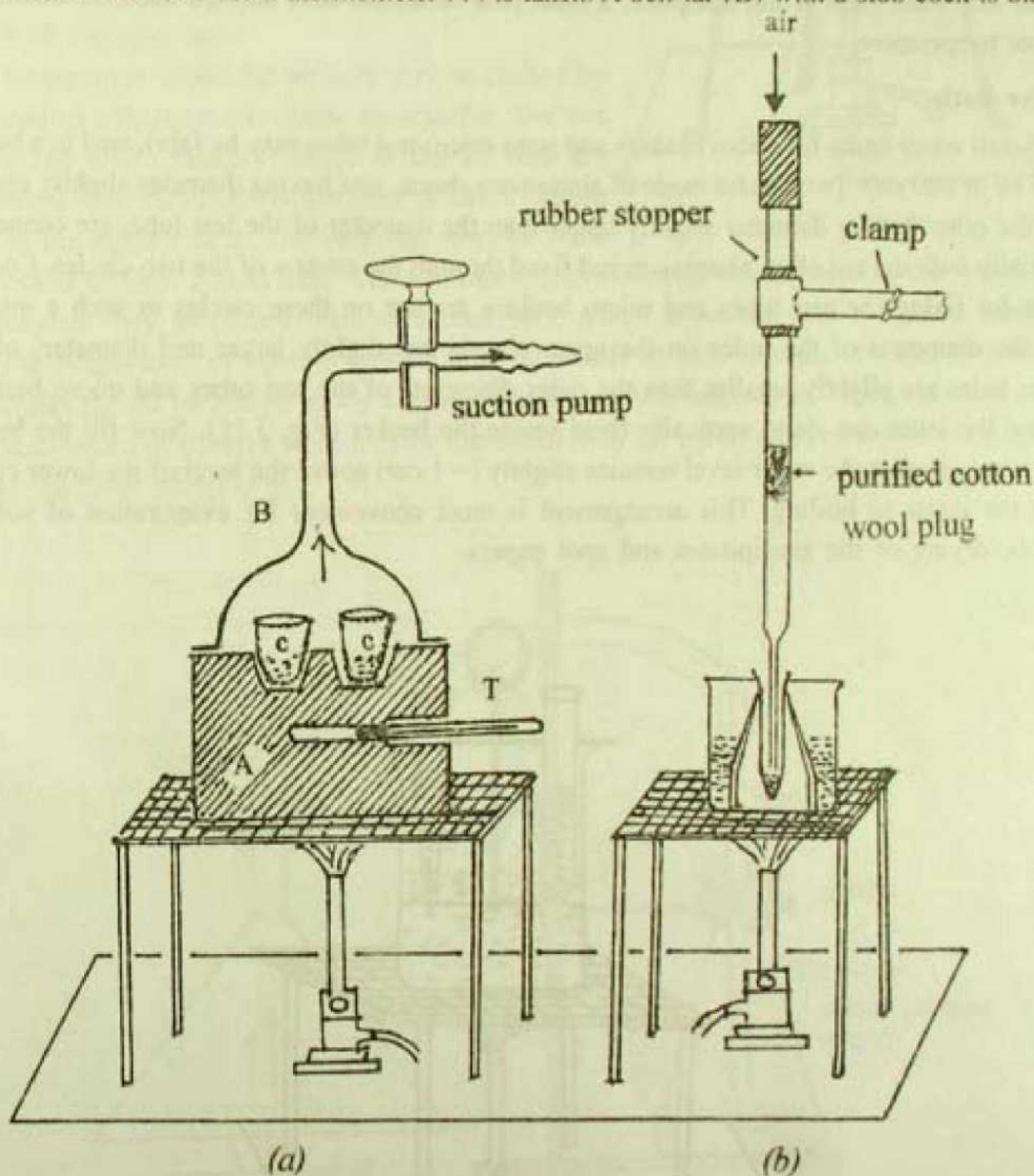


Fig. 3.14

on a well-fitted ground glass plate. The assembly thus functions as a small vacuum desiccator when the bell jar is connected with a suction pump through a regulator. The aluminium block

is gently heated and the suction pump is switched on. The liquid taken in the crucibles (C) are thus subjected to evaporation under reduced pressure at low temperature. When the volume of the liquid to be evaporated is small, it is even possible to evaporate the liquid while still in a semi-micro centrifuge tube or a test tube, placed in a hot water bath fabricated in a beaker ($\sim 250\text{ ml}$) provided with an adaptor cone for holding the tube (Fig. 3.14b). Dry air, filtered through a piece of clean cotton wool is blown over the surface of the liquid. If the temperature of the hot water bath is not adequate, a sand bath or an air bath may be used for heating at higher temperature.

Water bath

Small water baths for micro beakers and semi-micro test tubes may be fabricated in a beaker (250 ml or 400 ml). Two circles made of aluminium sheets, one having diameter slightly smaller and the other having diameter slightly larger than the diameter of the test tube, are connected coaxially with the aid of an aluminium rod fixed through the centers of the two circles. Coaxial holes for fixing the test tubes and micro beakers are cut on these circles in such a manner that the diameters of the holes on the upper circle are slightly larger and diameters of the lower holes are slightly smaller than the outer diameters of the test tubes and micro beakers, so that the latter can stand vertically fixed inside the beaker (Fig. 3.15). Now fill the beaker with water, so that the water level remains slightly ($\sim 1\text{ cm}$) above the level of the lower circle. Heat the water to boiling. This arrangement is most convenient for evaporation of volatile liquids, drying of the precipitates and spot papers.

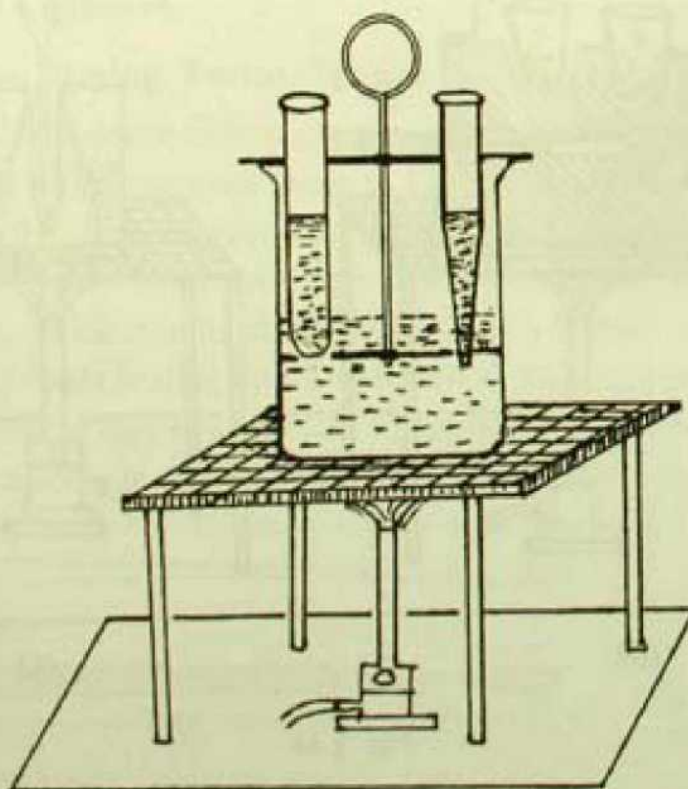


Fig. 3.15

Air bath

Air bath and sand bath are used for evaporation or heating at higher temperatures. A semi-micro air bath may be constructed inside a nickel crucible ($\sim 30\text{ ml}$) (C), put on a silica pipe triangle (T). The triangle supports the semi-micro beakers (B) or semimicro crucibles which are suspended inside the nickel crucible through a lateral slit (S) (Fig. 3.16) made of a copper wire.

Temperature inside the air bath may be checked by suspending a thermometer inside the crucible. The test tubes and micro beakers placed in the air bath are protected from very high temperature of direct heating due to the metal shield. The bath may also be filled

with sand to form a sand bath. The test tubes, micro beakers etc. containing the liquid to be evaporated, may be placed inside the sand bath, which is heated with a Bunsen burner.

For evaporation of volatile liquids, forming clouds of acid vapours or noxious gases, the apparatus should be placed inside a *Fume Cupboard*. Alternatively an arrangement of a hood for semi-micro qualitative work may be fabricated with the aid of an inverted funnel connected to an aspirator pump (Fig. 3.17).

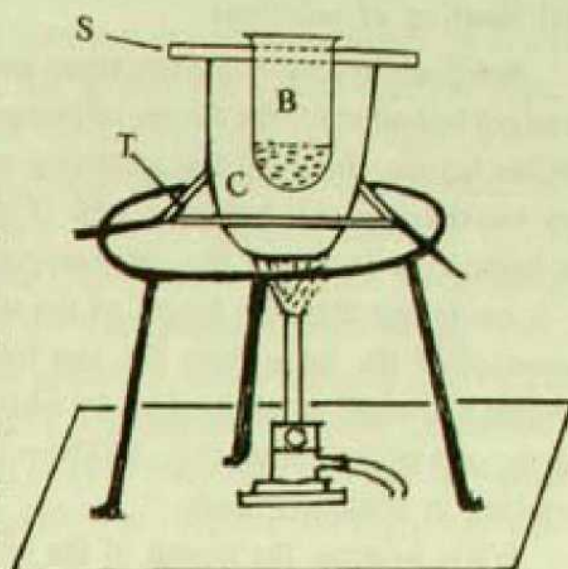


Fig. 3.16

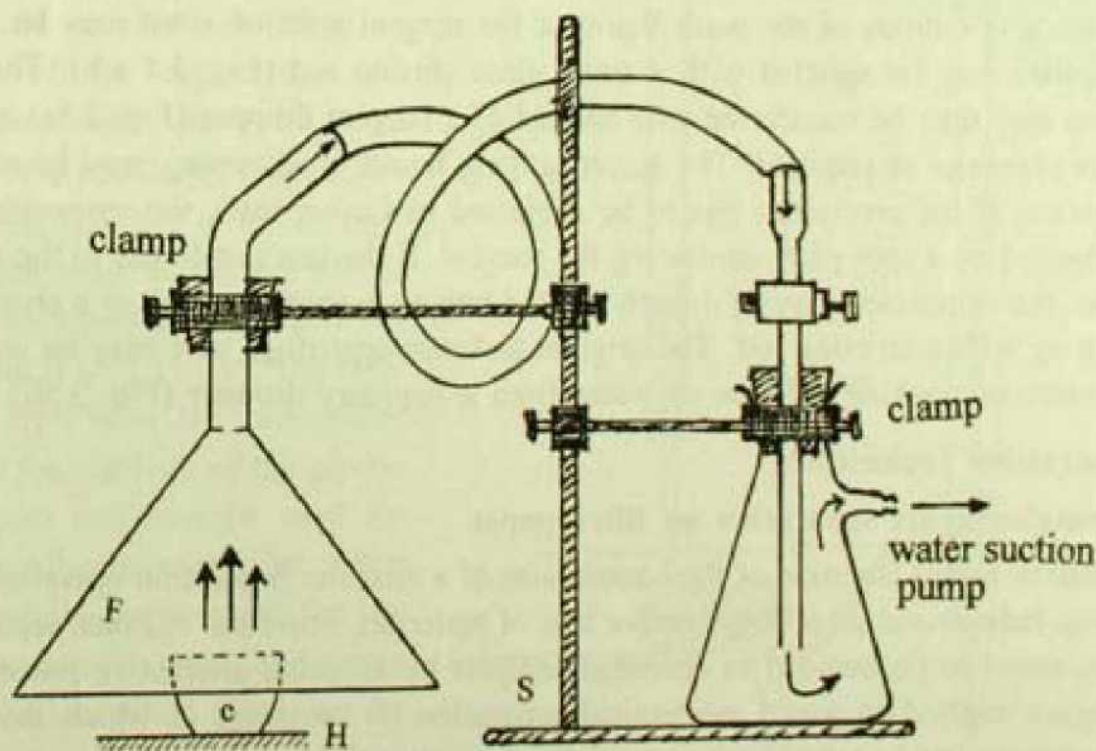


Fig. 3.17. F = inverted funnel, C = crucible, H = heater, S = stand

(e) Heating of solutions

Solutions in semi-micro test tubes and centrifuge tubes can not be boiled for the danger of bumping and spattering of hot liquids. Bumping and spattering may be minimized by inserting an anti bumping tube (Fig. 3.18a) into the solution. The length of the anti bumping tube should be $\sim 1\text{ cm}$ longer than the length of the test tubes for easy removal of the same from the test tube. The test tube should be heated on all its sides by whirling it around the flame of a micro burner (Fig. 3.18b) with constant gentle shaking in practiced hands.

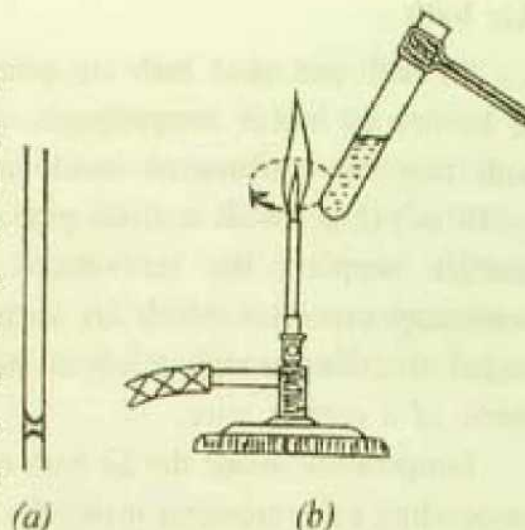


Fig. 3.18

While heating, the mouth of the test tube should be directed away from the others working nearby. However, safe heating for evaporation may be accomplished by placing the test tube with its contents on a steam bath or hot water bath (Fig. 3.15).

(f) Transferring of solid samples/reagents and precipitates

Solid samples and solid reagents may be transferred with the aid of small spatulas made of nickel or monel metal (Fig. 3.13 b,c). Small sized horn spatula are also very convenient for this purpose. Transferring of a precipitate from one container to another is difficult and needs skillful operation. In semi-micro qualitative analysis, actual transferring of a precipitate from a test tube or centrifuge tube to another is rarely necessary. However, when such transfer is essential, a few drops of the wash liquid or the reagent solution itself may be added and the precipitate may be agitated with a small glass stirring rod (Fig. 3.4 a,b). The resulting suspension may then be transferred with the aid of a reagent dropper (Fig. 3.5a) and ejected to another container as required. The accompanying liquid, if necessary, may be removed by centrifugation. If the precipitate has to be subjected to further tests, the suspension may be directly ejected on a spot plate containing the reagent. If the precipitate has to be evaporated to dryness, the suspension may be directly poured into an evaporating dish or a crucible, while still agitating with a stirring rod. The original test tube/centrifuge tube may be washed with a fine stream of washing solution or water from a capillary dropper (Fig. 3.5b).

3.5 Separation Techniques

(a) Chromatographic separation on filter paper

Separation means isolation of the constituents of a mixture. Separation operations are time consuming, tedious and invariably involve loss of materials. For these reasons, separations are always intended to be avoided in chemical analysis by adopting alternative procedures. The most elegant method to avoid mechanical separation, is *masking*, in which the undesired materials are rendered unreactive by transformation into soluble complexes or pseudosalts, by addition of auxiliary reagents. But in the analysis of unknown inorganic samples, separation often become unavoidable, particularly for classification or isolation of the unknown materials into certain analytical groups for subsequent spot test experiments.

Precipitation followed by filtration or centrifugation remains the standard and the most frequently used method of analytical separation. In spot test experiments, either by bringing together a drop of the test solution and a drop of the reagent on a drop reaction paper or by adding a drop of the test solution to a spot paper impregnated with the reagent, insoluble compounds are often precipitated directly on the filter paper itself. The soluble products along with unchanged materials, if any, in the test solutions, undergo *capillary diffusion* (cf. Sect. 2.5.1) and occur on the circular zone surrounding the precipitate. Thus, both precipitation as well as filtration are accomplished on the surface of the filter paper. Additional spot tests can even be conducted on the precipitate as well as on the circular zone surrounding it. Purification of the precipitate by washing with water or a suitable washing solution may be carried out by adding the washing liquid on the spot with the aid of a capillary tube or a capillary dropper. If the filtrate is not required for any additional test, the circular zone surrounding the precipitate may be completely removed by bathing the filter paper in the washing solution.

The spot may be fixed on the filter paper by drying. Drying fixes the precipitate more firmly in the cavities of the paper, so that the precipitate is not washed away by the washing liquid. But strongly acidic and strongly alkaline solutions can not be used for spot reactions on filter paper. More over, test requiring prolonged heating, or, those requiring larger volumes of liquids, can not be carried out on the filter papers.

(b) Cotton filters and filter tubes

When the precipitate is of no further interest, and the volume of the liquid is relatively large, a portion of the liquid may be withdrawn with the help of a pipette or a capillary dropper. The fine constricted end of the dropper or pipette may be closed with a wad of pure cotton wool drawn out to a point (Fig. 3.19 a,b). The clear liquid, free from the precipitate, ascends the capillary of the pipette or dropper and may be used for spot test after removing the cotton pad carefully and washing the tip.

Alternatively, a semi-micro sintered glass *filter tube* may be placed in a semi-micro test tube or a centrifuge tube of suitable size (Fig. 3.19c) and the combination may be subjected to centrifugation.

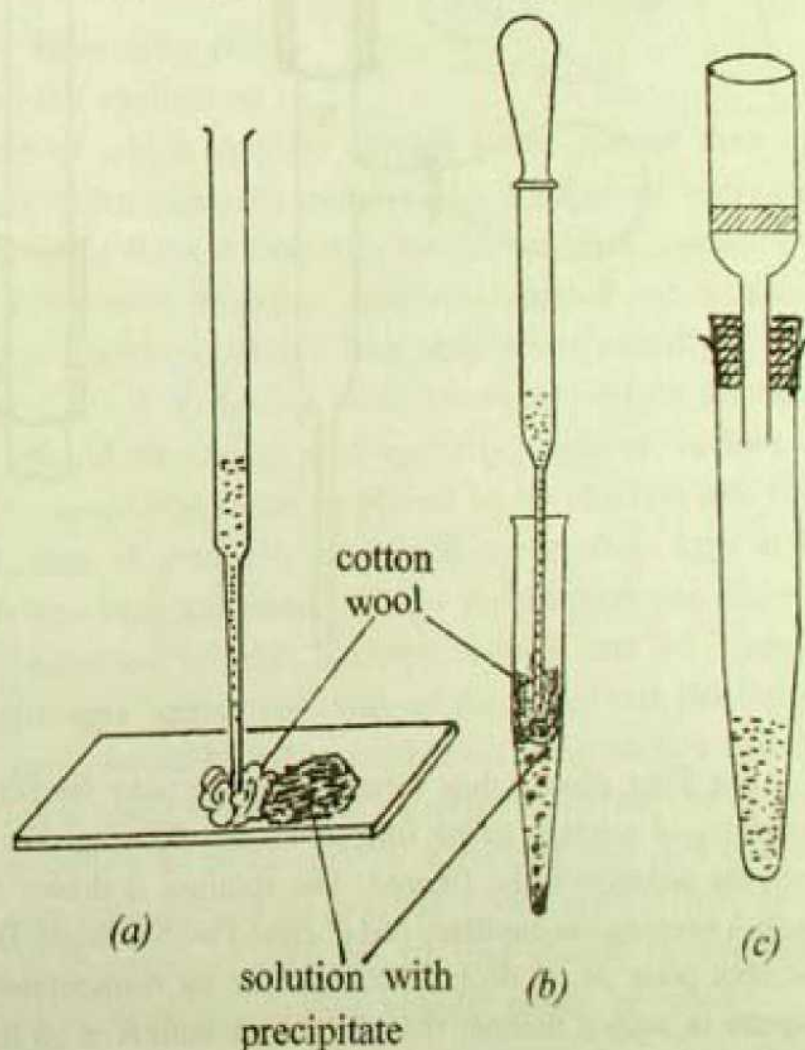


Fig. 3.19

The liquid is collected in the tube, while the precipitate remains on the sintered glass filter. Washing of the precipitate may be avoided by this technique.

(c) Hand suction filtering pipettes

A hand suction filtering pipette may be fabricated as follows. Take a 'T' shaped glass tube (short middle arm A, ~ 2-3 cm, two terminal long arms B+C, 10-12 cm, diameter ~ 5-6 mm) (Fig. 3.20). Attach a rubber bulb to the short arm A. The terminal arm B should be ground and flat. The arm C should be drawn into a fine capillary. Fix a short piece of rubber tubing D over the top of B. Take a filtering disc E or a circular piece of Whatman No. 1 filter paper strip of same diameter as the outer diameter of the tube B and place the same (E) on the flat ground surface of B. Support the disc E by placing another small glass tube F of the same diameter as B on it and fix B, E and F together by sliding the rubber tubing D, just far enough over E to hold when F is removed.

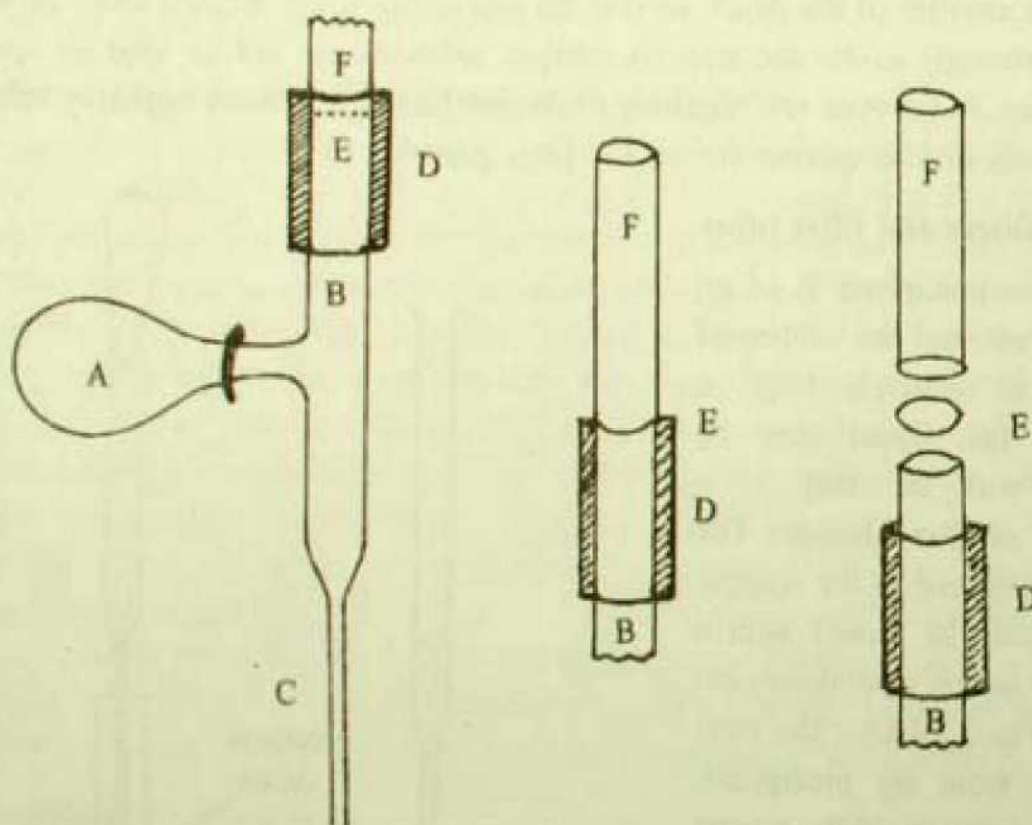


Fig. 3.20

The filter pipette thus formed, may be used for filtration either by placing drops of the solid liquid mixture to be filtered on the filtering disc E, or by immersing the tube end B into the solution to be filtered. The solution is drawn in to the tube on squeezing the rubber bulb A keeping the capillary end C closed with a finger. Drops of filtered liquid may be released on spot plate or on drop reaction paper by manipulating the bulb A and inverting the filter pipette in such a manner that the rubber bulb A is on top. The precipitate on the filter paper or the disc E may be withdrawn by sliding the rubber tubing D over the arm B.

(d) Emich filter sticks

Emich filter sticks (S) consist of a narrowed glass tube filter with an asbestos pad (A). The stick is fixed into a heavy wall suction tube (B) with the aid of rubber cork (C). A rubber bulb (D) is fitted with the delivery tube of B for suction (Fig. 3.21). A micro test tube receiver E for collecting the filtrate is placed inside the suction tube B in such a manner that the narrow end of the Emich filter stick tube (S) remains inside the receiver tube (E).

The solid liquid mixture to be filtered, is placed on the top of Emich filter stick, while keeping the rubber bulb (D) squized. On releasing the rubber bulb (D), the filtered liquid is collected into the receiver tube (E).

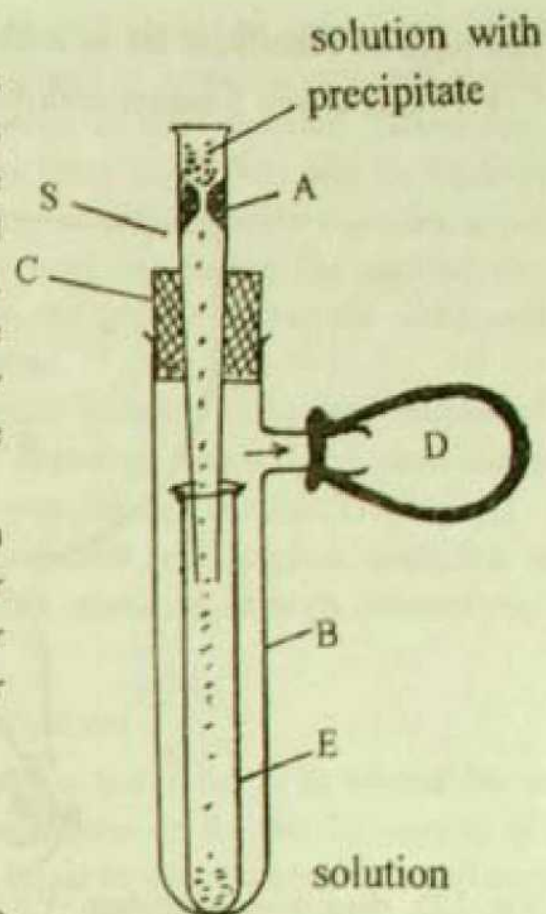


Fig. 3.21

(e) Centrifuge and Centrifugation

(i) Centrifuges

Centrifugation is a process of separating two substance, differing in density, with the application of centrifugal force, the magnitude of which may be several times greater than the gravitational force acting on these substances. In semi-micro qualitative inorganic analysis, separation of a precipitate from the solution may be conveniently carried out by centrifugation, which is much faster than filtration operation carried out in macro analysis. The liquid containing the precipitate is placed in a semi-micro centrifuge tube or in a semi-micro test tube (Fig. 3.1). In a similar tube, an equal weight of water is to be taken and the two tubes should be placed in diagonally opposite buckets of the centrifuge (Fig. 3.22, 3.23). The centrifuge cover is placed in its position and then rotation is started, slowly at first, then at gradually increased speed. It is kept at its highest speed for ~ 30-40 seconds and then switched off and the buckets are allowed to come to rest on their own. Rotation of the buckets should not be stopped mechanically, as this may cause agitation, leading remixing of the solid with the liquid. Before the start of centrifugation, care should be taken so that no solid parties adheres to the inner wall of the centrifuge tube. Since surface tension effects prevent the surface particles from settling, the mixture should be agitated with a stirring rod, any particle still adhering to the wall of the test tube should be washed down with a few drops of water with the aid of a capillary dropper and then the mixture should be subjected to centrifugation. Broken and cracked centrifuge tubes should never be used.

Two types of centrifuges are in common use :

- (1) Hand driven 2-bucket centrifuge with protecting bowl cover (Fig. 3.22).

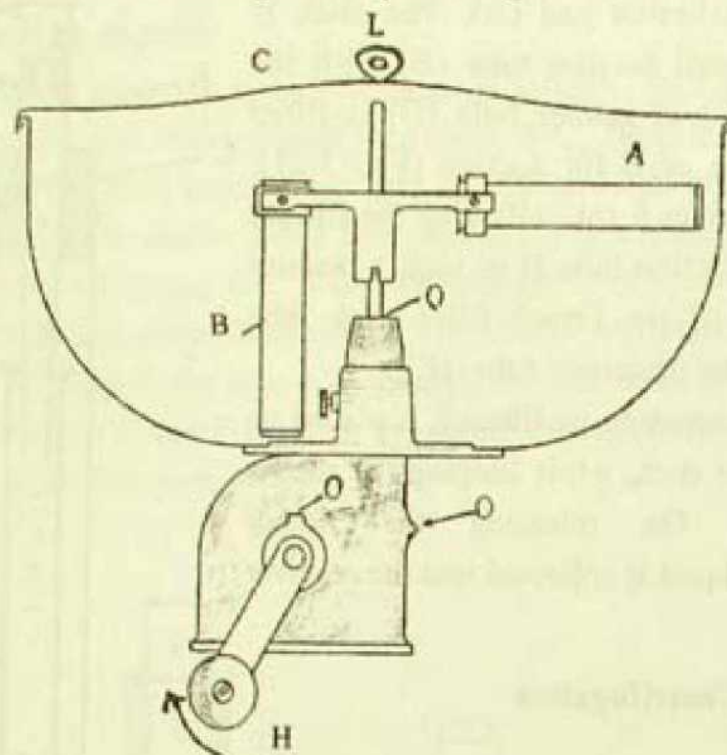


Fig. 3.22. Hand driven centrifuge. A = running position, B = resting position, C = removable lid, L = lifting knob for lid, H = operating handle, O = oiling hole.

- (2) Electrically driven variable speed centrifuge with protecting bowl cover (Fig. 3.23). These are of two types : (a) swing out bucket type (Fig. 3.23) and fixed angle bucket type. In the swing out type, the buckets swing out to horizontal position when the centrifuge is in operation. In the fixed angle type, the buckets remain fixed at angular position by means of rubber adapters, as such the instrument acts as an angle centrifuge.

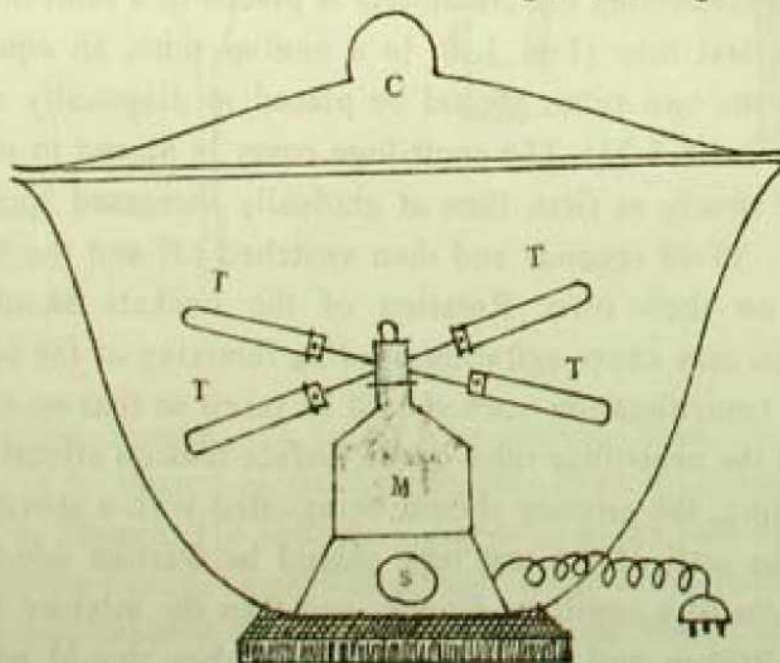


Fig. 3.23. Electrical centrifuge. T = tubes in running position, M = motor, S = control switch, C = removable lid.

Electrical centrifuge, after start, should never be left of. It should be immediately switched off if any unusual sound (due to breaking of glass tubes) or, vibration or heating effect is observed and the matter should be brought to the notice of the Laboratory Supervisors.

After centrifugation, the tubes are to be taken out from the buckets and the liquid is to be separated carefully with the aid of a capillary dropper or with a *transfer capillary*, avoiding stirring of the precipitate leading to remixing of the solid and liquid. The capillary should approach the bottom of the tube but should not touch the precipitate, nor the withdrawal of the capillary should cause any agitation in the solution.

Centrifugation is a much speedier operation than filtration. Since the precipitate is concentrated in a small volume at the bottom of the centrifuge tube or semi-micro test tube, the precipitate is clearly visible and its relative amount can be estimated (Fig. 3.24a)

The precipitate can be conveniently washed by repeated centrifugation, each time after stirring with the washing liquid. Even corrosive liquids, concentrated acids, alkalies may be easily manipulated in practiced hands.

(ii) Collecting Centrifugate and Washing of the Precipitates

When the precipitate has to be subjected to a chemical test, it has to be washed free from the adhering solution to avoid contamination and interference in the test. In majority of the cases, in qualitative inorganic analysis, the washing liquid is water, containing small amount of the precipitant for common ion effect. Some times, dilute solution of an indifferent electrolyte, such as ammonium nitrate is added to check the formation of colloidal materials through *peptization* of the precipitate.

After centrifugation, the precipitate collects at the bottom of centrifuge tube (Fig. 3.24a,b). The centrifugate may be collected from the centrifuge tube with aid of a capillary dropper or with a transfer capillary (Fig. 3.24 c,d). The precipitate should not be agitated in removing the centrifugate. The dropper or transfer capillary should be pushed toward the bottom of the solution in the manner that the point of the capillary always remains just below the surface of the liquid.

The operation should be repeated until the entire solution is collected in the dropper and the dropper tip should be held ~ 1 mm above the precipitate. The supernatant liquid may be collected in a clean test tube with the aid of a dropper pipette.

For washing of the preppitate while still in the centrifuge tube, add 8-10 drops of distilled water or other washing liquids as necessary, shake or stirr the mixture thoroughly using a glass stirring rod or a

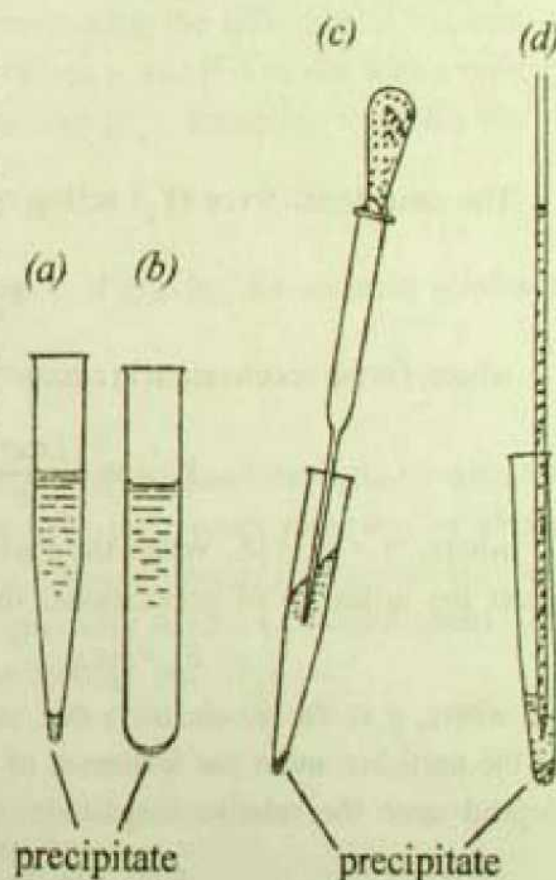


Fig. 3.24

platinum wire. Then centrifuge the mixture by counter balancing the centrifuge tube against another of the same kind containing water up to the same level as the test solution. The first washing may be mixed with the centrifugate, whereas, the subsequent washings may be discarded in the manner just described. The operation may be repeated two to three times to ensure complete washing.

(iii) Theoretical Basis of Centrifugation

When a mixture of suspended solid particles and a liquid is subjected to centrifugation, the particles settle to the bottom of the liquid at a much faster rate than their normal rate of settling under the influence of gravity. Suppose particles of average mass ' m ' grams are suspended in a liquid. When subjected to centrifugation, the solid particles move in a circle of radius, ' a ' cm and make ' n ' number of revolutions per second (Fig. 3.25.).

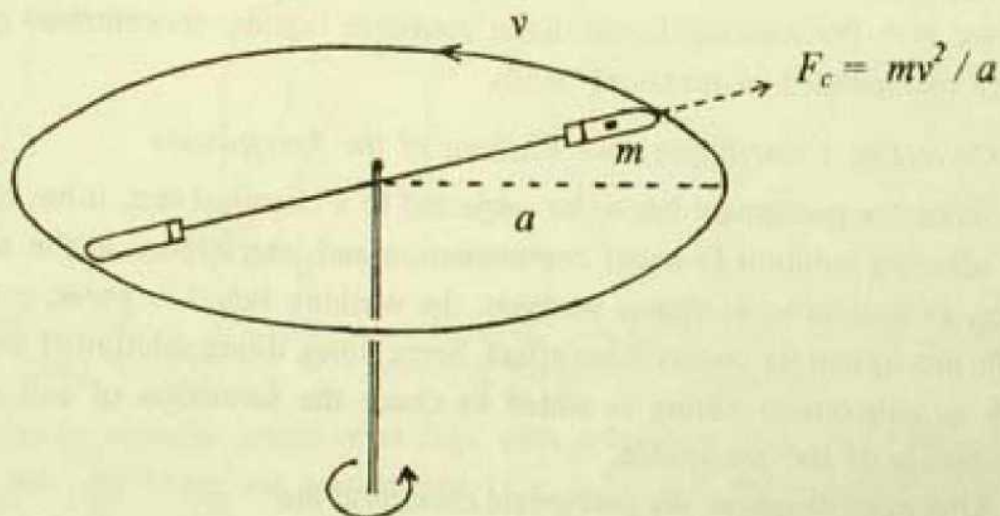


Fig. 3.25

The centrifugal force (F_c) acting on the particles will be,

$$F_c = m.f. = \frac{mv^2}{a}$$

where, f is the acceleration in $cm.sec^{-2}$, v is the velocity in $cm.sec^{-1}$. Since, $v = 2\pi an$, therefore,

$$F_c = m \cdot \frac{(2\pi an)^2}{a} = m \cdot 4\pi^2 a \cdot n^2$$

where, $\pi = 3.1416$. When the particles are in resting position, they tend to settle down under the influence of gravitational force (F_g), defined as,

$$F_g = m.g$$

where, g is the acceleration due to gravity = $981 cm.sec^{-2}$. The relative rates of settling of the particles under the influence of centrifugal force (F_c) and gravitational force (F_g) will depend upon the relative magnitudes of the two forces :

$$\frac{F_c}{F_g} = \frac{m \cdot 4\pi^2 a n^2}{m \cdot g} = \frac{4\pi^2 a n^2}{g}$$

If the centrifuge makes N revolutions per minnute (R.P.M.), then the number of revolutions per second (n) will be equal to, $(N/60)$.

$$\therefore \frac{F_c}{F_g} = \frac{4\pi^2 a (N/60)^2}{g} = \frac{4(3.1416)^2 a N^2}{(981)(60)^2} = 1.118 \times 10^{-5} a N^2$$

If the centrifuge revolves in a circle of 15 cm radius at a speed of 1725 R.P.M., the above ratio will be,

$$\frac{F_c}{F_g} = 1.118 \times 10^{-5} \times 15 \times (1725)^2 \approx 499 \approx 500$$

$$\therefore F_c \approx 500. F_g$$

Thus, the centrifugal force (F_c) will be ~ 500 times stronger than the gravitational force (F_g). So the time for settling under the influence of centrifugal force will be $(1/500)$ th. of the time for settling under gravity. If a particle takes ~ 10 minutes to settle under gravity, it will settle within $(10/500)$ minutes, or $(10 \times 60/500)$ seconds i.e., ~ 1.2 seconds on centrifugation in the above mentioned centrifuge.

Now, when a solid particle moves through a liquid, as in the case of settling of a precipitate, the thin layer of the liquid, that is in immediate contact with the solid, is virtually stationary, just as the flow of a liquid through a tube. As a result, a viscous force of resistance (viscous drag) is exerted on the moving solid. A steady force must, therefore, be acting on the particle in order to maintain a uniform downward velocity, overcoming the influence of viscosity of the liquid. If the moving particle is a spherical solid of radius, r , and if it moves with a velocity, u , through a liquid of viscosity coefficient, η , viscous drag (F_v), according to *Stokes law*, is given by,

$$F_v = 6\pi\eta ru$$

When such a spherical body falls under the influence of gravity, the constant downward force (F_g) acting on the body is given by,

$$F_g = \frac{4}{3} \pi r^3 (\rho_s - \rho_l) g$$

where, ρ_s and ρ_l respectively are the densities of the falling solid and the virtually stationary liquid, through which the solid falls, the other terms have their usual meanings as already described. Stokes equation indicates that the opposing force of viscosity (F_v) increases with increase of velocity (u) of the settling particle, which gradually attains a constant speed when the viscous drag (F_v) is exactly balanced by the gravitational pull (F_g) i.e.,

$$6\pi\eta ru = \left(\frac{4}{3} \pi r^3\right) (\rho_s - \rho_l) g$$

Thus, the velocity (u) of the falling body is given by,

$$u = \frac{2gr^2(\rho_s - \rho_l)}{9\eta}$$

In case of settling down of a precipitate in a test tube containing the solid and a liquid, u is the uniform rate of settling. As the above relation implies, the rate of settling of a precipitate will increase with:

- (i) increase of particle size (r),
- (ii) increase of the density difference ($\rho_s - \rho_l$) between the falling solid and the virtually stationary liquid,
- (iii) decrease of viscosity coefficient (η) of the liquid,
- (iv) increase of acceleration due to gravity (g).

Although the influences of the above mentioned factors are comparatively small, but it is observed that fine crystalline compounds, in contact with the solution in which they are precipitated, tend to grow in size, particularly when the solution is kept at an elevated temperature, readily sink down or settle down on occasional shaking or stirring the solution, or on addition of electrolytes. Heating to boiling temperature of the solution also accelerates settling. Increase of temperature lowers the viscosity (η) of the liquid and also increase the density difference ($\rho_s - \rho_l$) between the solid and the liquid.

Thus, stirring, warming and heating to boiling accelerate settling and so the solution should be subjected to any of these operations before proceeding to centrifugation.

(f) Other methods of separation

Principles of chromatography, ion-exchange, solvent extraction, and electrographic methods as applied to qualitative inorganic analysis, have been briefly discussed in Chapter-2, and these will not be repeated here.

3.6. Identifying Gases

Qualitative inorganic analysis involve three kinds of manipulation with gases and vapours:

- (i) Gases (vapours) employed as reagents for precipitation, acid-base and oxidation-reduction reactions.
- (ii) Gases (vapours) liberated as reaction products that are subsequently identified by their characteristic chemical tests.
- (iii) Distillation of certain reaction products that are subsequently identified by their chemical tests.

Consequently, the apparatus for manipulation of gases (vapours) depend upon the purpose intended.

(a) Gases as reagents

In qualitative inorganic analysis, gases such as H_2S , SO_2 , Cl_2 , NH_3 , CO_2 are frequently used as reagents. Apparatus for generation, storing of H_2S , SO_2 and Cl_2 gases and their aqueous solutions have been described in section 3.3. Ammonia gas, as and when required for inorganic qualitative analysis, may be used by holding the test materials in a filter paper strip over an open bottle of concentrated ammonia inside a *Fume Cupboard*. CO_2 gas if necessary, may

be generated by the reaction of sodium carbonate or calcium carbonate with dilute hydrochloric acid in an apparatus similar but much smaller in size to that employed for preparation of SO_2 or Cl_2 gas.

Spot reactions on paper involving the reaction of the test materials with reagent gases such as H_2S , SO_2 , NH_3 , halogens (Cl_2 , Br_2) and steam may be carried out by using mini gas generators or *streamers*, made of a hard glass test tube or a small conical flask having a side arm and fitted with a fine capillary tube at its mouth with the aid of a rubber cork (Fig. 3.26). The gases generated within the streamer are lead to a strip of filter paper impregnated with the test solution and placed on the open mouth of the side arm. If necessary, the contents of the streamer may be gently warmed.

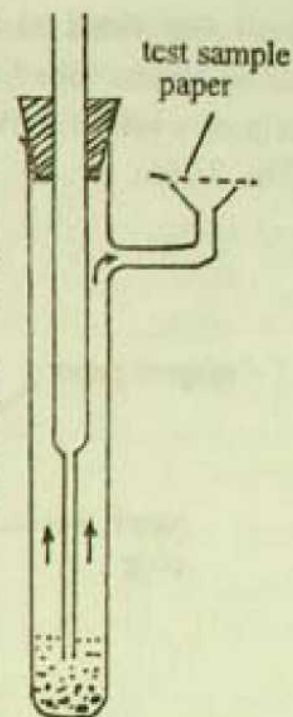


Fig. 3.26

(b) Identification of gaseous reaction products

Apparatus for detection of gaseous reaction products such as H_2S , SO_2 , NH_3 , AsH_3 , Cl_2 , Br_2 , NO_2 , CrO_2Cl_2 etc. liberated from the reactions of sulfide, sulfite/sulfate, ammonium salts, nitrates/nitrites, arsenic

compounds, halides etc. with appropriate reagents are shown in Figs. 3.27 and 3.28. These apparatus may be designed in semi-micro test tubes (5-10 ml). In the simplest type of these apparatus (Fig. 3.27a), the test material is treated with acid or alkali and or other reagents in a 5-10 ml semi-micro test tube. A piece of clean cotton wool plug is placed near the mouth of the test tube. A small filter paper strip impregnated with the appropriate reagent is held

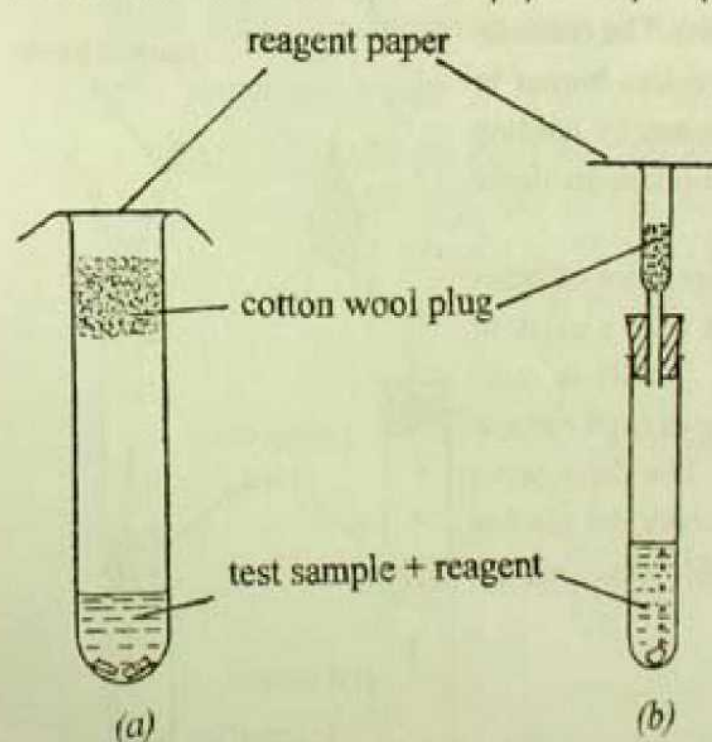


Fig. 3.27

at the mouth of the test tube. In another modification (Fig. 3.27b) a small piece of glass tube may be fixed with the aid of rubber cork at the mouth of the test tube containing the test material and the attacking reagents. A small piece of clean cotton wool plug is inserted inside the glass tube. The reagent paper is held at the mouth of the glass tube. The reagent paper may also be brought into contact with the gaseous products by hanging the same inside the reaction tube or flask (Fig. 3.28 a,b) with the aid of a platinum wire loop. The contents of the test tube is gently warmed if necessary to facilitate gas evolution. The gases evolved from the reaction inside the test tube is absorbed in the reagent paper and give

the characteristic observations. The reagent paper strips may also be hung inside the reaction tube containing the test material and the attacking reagents. To avoid contamination due to bumping and spattering, the reagent paper may be placed inside a glass tube with a cotton

wool plug, fitted inside the reaction tube with the aid of a rubber cork (Fig. 3.29a). With the aid of a glass tube having a capillary head, fixed at the mouth of the reaction tube with the help of a rubber cork, a drop of a liquid reagent may also be hung inside the reaction tube (Fig. 3.29b).

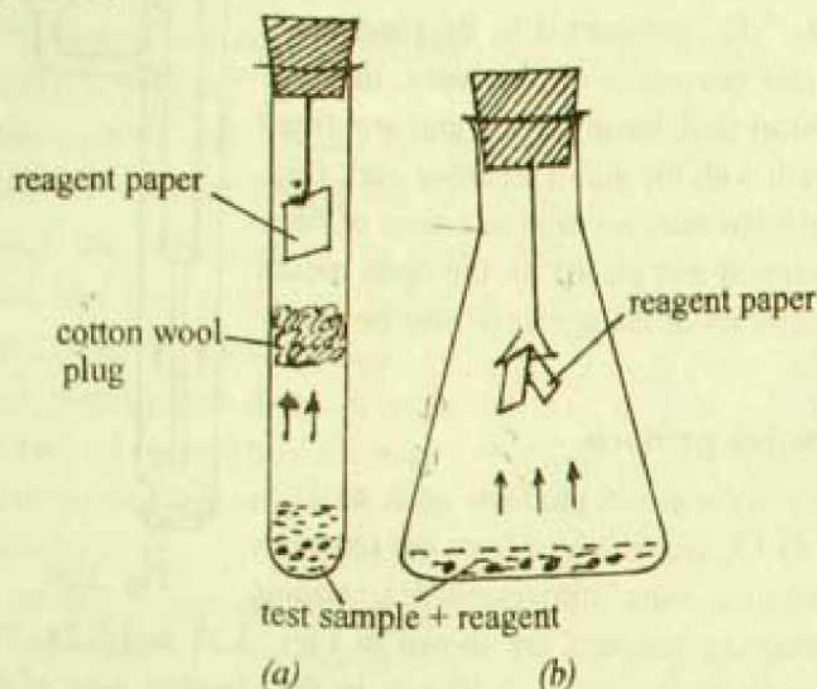


Fig. 3.28

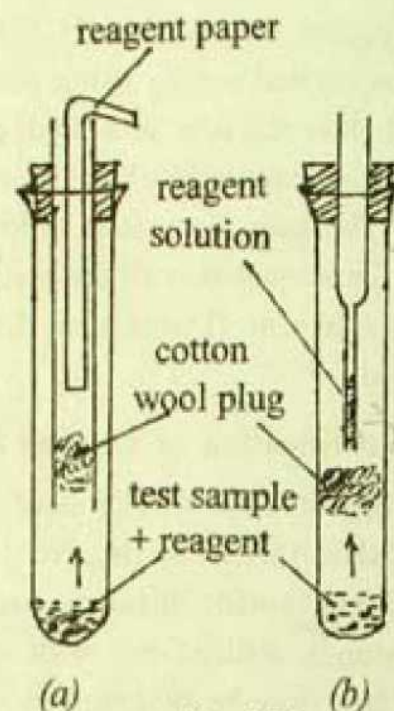


Fig. 3.29

If the gaseous product is inflammable, it may be ignited at the head of an angular glass tube fixed at the mouth of the reaction tube with the aid of a rubber cork (Fig. 3.30a). A cotton wool plug may be inserted inside the reaction tube. The contents of the reaction tube may be heated on a semi-micro burner to facilitate gas evolution and the gas may be ignited by holding the mouth of the angular glass tube near the non-luminous flame of the burner.

For identification of a gaseous product in presence of other indifferent gases, a semi-micro test tube fitted with a glass or rubber stopper, attached with a funnel (Fig. 3.30b) is most convenient. A filter paper impregnated with the desired reagent is attached to the funnel fixed to the stopper. The filter paper permits the passage of the indifferent gases, whereas, the gas that reacts with the reagent is only retained and identified by subsequent spot test.

(c) Semi-micro distillation

A semi-micro test tube (T), fitted with a delivery tube, doubly bent at right angles (Fig. 3.31) may be used as a distillation apparatus. A micro test tube or a small crucible containing a suitable absorbing liquid (A) for the issuing gas

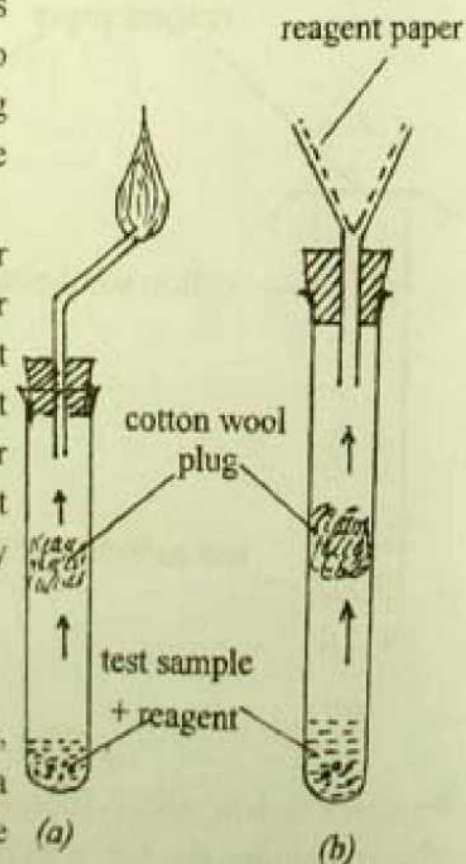


Fig. 3.30

may serve as a receiver (R). The absorbed gas may then be identified by the colour of the product it forms with the absorbing reagents, or the solution resulting from absorption of the gas may be transferred on to a spot plate or a filter paper strip for further tests.

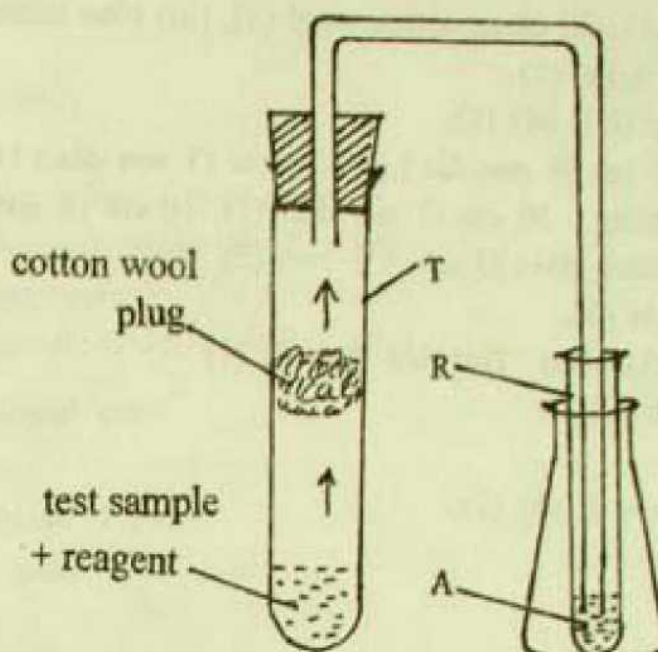


Fig. 3.31

3.7. Workbench Apparatus, Equipment and Reagents

The following apparatus, equipment are and reagents required for each workbench in a semi-micro qualitative inorganic analysis laboratory.

(a) Glass, porcelain wares

1. Wash bottle with jet (250 ml, 100 ml) [Fig. 3.7]
2. Beakers : 250 ml (1), 100 ml (1), 50 ml (1), 25 ml (1), 10 ml (1).
3. Conical flasks : 50 ml (1), 25 ml (1), 10 ml (1).
4. Test tubes : 7.5 cm × 1 cm (4 ml) with rim (6), without rim (2).
5. Filtering apparatus (Figs. 3.19, 3.20, 3.21 one each).
6. Gas identifying apparatus (Figs. 3.26-3.32, one each).
7. Droppers complete with teats and rubber bulbs : medicine type (2), reagent type (2), capillary type (2), [Fig. 3.5].
8. Centrifuge tubes (3 ml) (4).
9. Boiling tubes (6 cm × 2.5 cm, ~ 20 ml) (2).
10. Anti bumping tube (1) [Fig. 3.18].
11. Wooden stand for test tubes (1), for droppers (1).
12. Spot plate (6 cavities) (1).
13. Watch glass (3.5 cm dia) (1).
14. Measuring cylinder (5 ml) (1).
15. Funnel (3 cm) (1)

16. Capillary tubes.
17. Evaporating dish (1).
18. 25 ml wide mouth stoppered bottles filled with: (i) 2 cm × 2 cm filter paper strips for drop reaction (1), (ii) clean cotton wool (1), (iii) blue litmus paper strips (1), (iv) red litmus paper strips (1).
19. Porcelain crucible (6-8 ml) (1).
20. Glass tubing : 30 cm (4 mm dia.) (1), 10 cm (3 mm dia.) (1).
21. Glass rod for stirring : 30 cm (3 mm dia) (1), 10 cm (3 mm dia.) (1).
22. Cobalt (double blue) glass (3 cm × 3 cm) (2).
23. Silica pipe triangle (1).
24. Dropping bottle (labelled "Distilled Water") (1).
25. Microscope slides (2).
26. Fusion tubes (6).
27. Mica foils (2 cm × 2 cm) (2).
28. Mortar pastle (1).

(b) Metallic utensils

1. Platinum wire (5 cm of 0.3 mm dia.) (1).
2. Semi-micro metallic spatula (2) [Fig. 3.13].
3. Forcep (10 cm) (1)
4. Test tube holder (1) [Fig. 3.2].
5. Test tube brush (1) [Fig. 3.2].
6. Pipe cleaner.
7. Tripod stand with wire gauge (1) for water bath [Fig. 3.15].
8. Nickel crucible for fusion and air bath [Fig. 3.16].
9. Hot block (1) [Fig. 3.14].
10. Burners : Bunsen type (1), semi-micro type (1)
11. Tongs (1)
12. Air bath (1) [Fig. 3.16].
13. Water bath (1) [Fig. 3.15].
14. Lead crucible with lid (1).

(c) Rubber goods

1. Rubber stoppers/corks for conical flasks, test tubes, gas absorption tubes etc. (1 cm × 1 cm) (2), (1.5 cm × 0.5 cm) (2).
2. Rubber tubings : (10 cm × 3 mm) (1) for connecting glass tubes, (5 cm × 5 mm) for filter tubes.

(d) Equipment for common use

1. Centrifuge (hand operated/electrically driven)
2. Water bath (gas heated/electrically heated)

3. Water suction pumps
4. Fume cupboard
5. Hair dryer
6. Hot plate/sand bath
7. Table brush
8. Hot air oven (110°C)
9. Cooling blocks
10. Cation and anion exchange resin columns.
11. Apparatus for electrophoresis (for P.G. lab.)
12. Apparatus for electrography (for P.G. labs.)
13. Microscope (students model) (for P.G. lab.)

(e) Equipment for personal use

1. Apron (1)
2. Eye protecting glass (1 pair)
3. Hand gloves (1 pair)
4. Small towel (2)

(f) Workbench reagents

Table 3.2. : Most frequently used liquid reagents.

Reagents to be kept in glass stoppered bottles (Fig. 3.6e)

<i>Acids</i>	<i>Concentrated</i>	<i>Dilute</i>
Hydrochloric Acid	12 M	6M, 2M
Sulfuric Acid	18 M (36N)	9M, 4M, 1M
Nitric Acid	16 M	6M, 2M, 1M
Acetic Acid	17 M	

Reagents to be kept in bottles fitted with reagent droppers [Fig. 3.6 a,b].

<i>Reagent</i>	<i>Concentration</i>	<i>Reagent</i>	<i>Concentration</i>
Sodium hydroxide	2 M	H ₂ S-water	0.1 M
Conc. ammonia	15 M	Barium chloride	0.25 M
Dil. ammonia	2 M	Silver nitrate	0.1 M
Dil. acetic acid	2 M	Ferric chloride	0.5 M
Potassium hydroxide	2 M	Potassium chromate	0.1 M
Ammonium sulfide	1 M	Potassium ferricyanide	0.033 M
Ammonium carbonate	1 M	Potassium ferrocyanide	0.025 M
Disodium hydrogen phosphate	0.033 M	Ammonium thiocyanate	0.1 M

3.8. Do's and Don'ts :

Healthy Laboratory Practices and Precautions

1. Keep your working bench neat and clean. Use a string duster to wipe up the liquid drops and solid particles from the working bench. Clean the glass and porcelain wares by washing with water or with a suitable liquid as required, finally wash with distilled water.
2. Do not keep the reagent bottles open and do not leave the reagent droppers and reagent bottle stoppers on the working bench, as these may contaminate the reagents. Keep a $\sim 15\text{ cm} \times 15\text{ cm}$ clean glass plate on the working bench for this purpose and clean it after use every time. After using a reagent, the reagent bottle should be closed with its stopper or the dropper and kept in the proper place on the rack.
3. Avoid misuse of chemicals, water and gas supply. Adjust the size of the Bunsen flame as required. The burner should be extinguished when heating is not required. Do not keep the water taps open when these are not in use. Use droppers, spatulas, spoons etc. for transferring chemicals so as to avoid the use of unnecessary excess of reagents. Do not use filter paper strips for transferring chemicals.
4. Do not throw filter paper strips or broken test tubes or any other solid object on the wash basin, sinks, floor, or in water outlets, since these may eventually clog the waste water flow. Waste solid materials should be thrown into a bucket maintained for this purpose and kept at a corner of the laboratory.
5. Strong acids and strong bases should not be directly thrown into the sink, which may be damaged by these reagents. Before throwing into the sink, dilute the strong acids and strong bases with large volumes of water and then flush out through the sink with much water.
6. Wear apron whenever working in the laboratory. Use hand gloves and wear eye protecting glasses when working with hazardous chemicals and doing reactions involving liberation of gases, vapours, fumes etc. Do not eat or drink anything while working in the laboratory. Clean your hands and faces thoroughly before taking any food after working in the laboratory.
7. Carry out all operations involving (i) evaporation of concentrated acids, (ii) evaporation to dryness or decomposition of ammonium salts, ferrocyanide, ferricyanide, thiocyanate, nitrate and nitrite salts, (iii) removal of borate, silicate, fluoride etc. and all other reactions involving evolution of poisonous gases and vapours of disagreeable odours, (iv) reactions involving the passage of hydrogen sulfide gas or addition of H_2S -water, SO_2 -water etc. and their removal from the solution, (v) digestion with concentrated acids, aqua regia etc. positively inside a **Fume Cupboard** provided with adequate exhaust arrangement.
8. In carrying out a reaction involving formation of a precipitate, ensure that both the test solution and the reagent solution are absolutely free from suspended particles, otherwise, filter the solutions before carrying out the test.

9. Have a clear knowledge about the chemical basis of the tests being carried out, otherwise, it will be difficult to maintain the proper reaction conditions required for a particular test and there shall be ample chance for committing mistakes leading to wrong detection.
10. Record all your experiments, observations and inferences, positive or negative or inconclusive what so ever, in your laboratory note book date wise, in a systematic manner, as soon as the test is performed. Under no circumstances, recording of the experiments and observations should be postponed until leaving the laboratory. Such a good practice should be developed right from the very out set in the interest of accurate recording of the first hand observations, devoid of any inaccuracy, that may creep in building the "story" after leaving the laboratory. If the analysis remains incomplete at the end of a laboratory hour, label all the solutions and precipitates clearly. Cover these with a glass jar or a big size inverted funnel or a large size beaker to protect these from dust and other contaminations.

CHAPTER - 4

Reactions of Cation Radicals

4.1 Introduction and Classification of Cation Radicals

There are two types of procedures for the detection of cation radicals: (i) systematic group analysis followed by unambiguous confirmatory tests and (ii) individual tests by semi-micro methods using spot test techniques, based on elimination, masking-demasking reactions, chromatographic separations etc. The systematic group separation method is simple and is most suitable for the beginners, but it is laborious, requires large quantities of chemicals and above all, this procedure is a bit dirty and polluting. Semi-micro tests, on the other hand, are much cleaner, require less chemicals, but it requires high experimental skill and sound knowledge in chemistry of the elements and their compounds along with the fundamental basis of different aspects of inorganic reactions, particularly the equilibria involving acid-base, oxidation-reduction, precipitation and complex formation reactions (*cf.* Ch-2). This chapter deals with the chemical reactions of the individual cation radicals with some typical as well as special reagents. Indication, identification and finally confirmation of the radicals in unknown materials will be based on these reactions.

Based on the insolubility of some common compounds such as, chlorides, sulfides, hydroxides, carbonates, phosphates etc., the common cation radicals are classified into five analytical groups, viz., Group-I to Group-V; as summarised below:

Groups	Group Reagents	Group Properties	Metal ions
I	Dilute HCl	Sparingly soluble chlorides	$\text{Ag}^{\text{I}}, \text{Hg}^{\text{I}}, \text{Pb}^{\text{II}}$ $(\text{WO}_3 \cdot x\text{H}_2\text{O})^*$
II	Dilute HCl + H_2S	Sparingly soluble sulfides	$\text{Hg}^{\text{II}}, \text{Pb}^{\text{II}}, \text{Bi}^{\text{III}}, \text{Cu}^{\text{II}},$ $\text{Cd}^{\text{II}}, \text{As}^{\text{V/III}}, \text{Sb}^{\text{V/III}},$ $\text{Sn}^{\text{IV/II}} (\text{Mo}^{\text{VI}}, \text{V}^{\text{V}})^*$
IIA	$(\text{NH}_4)_2\text{S}_x$	Sulfides do not dissolve	$\text{Hg}^{\text{II}}, \text{Pb}^{\text{II}}, \text{Bi}^{\text{III}}, \text{Cu}^{\text{II}}$ $\text{Cd}^{\text{II}}, (\text{Mo}^{\text{VI}})^* \text{ traces}$
IIB	$(\text{NH}_4)_2\text{S}_x$	Sulfides dissolve	$\text{As}^{\text{V/III}}, \text{Sb}^{\text{V/III}}, \text{Sn}^{\text{IV/II}}$ $(\text{Mo}^{\text{VI}})^*$
IIIA	$\text{NH}_4\text{Cl} + \text{aq. NH}_3$	Hydroxides precipitate	$\text{Fe}^{\text{III}}, \text{Cr}^{\text{III}}, \text{Al}^{\text{III}},$ $\text{Mn}^{\text{IV/II}}, (\text{Ti}^{\text{IV}}, \text{Zr}^{\text{IV}},$ $\text{Be}^{\text{II}}, \text{Ce}^{\text{IV}}, \text{Th}^{\text{IV}}, \text{U}^{\text{VI}})^*$

*Rare element (*cf.* Ch-8)



Groups	Group Reagents	Group Properties	Metal ions
IIIB	$\text{NH}_4\text{Cl} + \text{aq. NH}_3 + \text{H}_2\text{S}$	Sulfides precipitate	$\text{Co}^{\text{II}}, \text{Ni}^{\text{II}}, \text{Mn}^{\text{II}}, \text{Zn}^{\text{II}}$
IV	$\text{NH}_4\text{Cl} + \text{aq. NH}_3 + (\text{NH}_4)_2\text{CO}_3$	Carbonates precipitate	$\text{Ba}^{\text{II}}, \text{Sr}^{\text{II}}, \text{Ca}^{\text{II}}$
V	$\text{NH}_4\text{Cl} + \text{aq. NH}_3 + \text{Na}_2\text{HPO}_4$	Phosphate precipitates No precipitation	Mg^{II} May be $\text{Na}^+, \text{K}^+, \text{NH}_4^+$

4.2 Reactions of Silver (Ag^{I})

Indication

(1) Blackening by sodium stannite solution

Sodium stannite (Na_2SnO_2) solution reduces silver compounds to black metallic silver.



Place a grain of the white solid sample (or aqueous or dil. HNO_3 solution of the sample) on a spot plate and add a drop of freshly prepared sodium stannite solution. Immediate blackening is observed if Ag^+ is present.

NB. Mercury (Hg^{I} and Hg^{II}) and bismuth (Bi^{III} , and Bi^{V}) give similar tests.

(2) Blackening by sodium sulfide solution or H_2S - water

Place a grain of the white sample (or aqueous or dil. HNO_3 solution of the sample) on a spot plate and add a drop of Na_2S solution or H_2S -water. Immediate blackening occurs due to the formation of silver sulfide, Ag_2S .



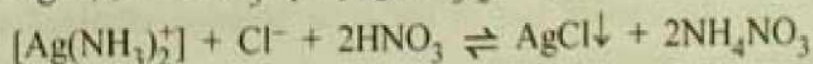
N.B. Pb^{2+} , Hg^{2+} , Hg_2^{2+} , Cu^{2+} , Bi^{3+} give similar tests and interfere.

(3) Dilute HCl solution

To 1-2 drops of aqueous or dil. HNO_3 solution of the sample, add 1 drop of dil. HCl . Curdy white precipitate of AgCl appears:



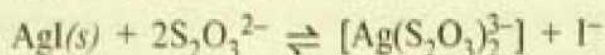
Centrifuge the precipitate and reject the centrifugate with a dropper. Add 1-2 drops of aqueous NH_3 solution to the precipitate. The precipitate passes into solution due to the formation of diammineargentate $[\text{Ag}(\text{NH}_3)_2]^+$ complex ion, but reappears on addition of dil. HNO_3 (~2M)



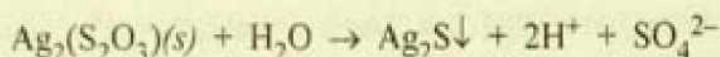
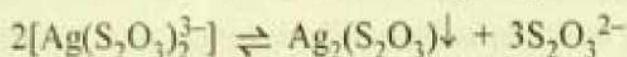
Caution: Solution obtained after dissolving the precipitated AgCl in $aq\text{-NH}_3$ solution should be immediately acidified with dil.HNO_3 and disposed of. If the ammoniacal solution of the $[\text{Ag}(\text{NH}_3)_2]^+$ complex is set aside, silver nitride, Ag_3N , (*fulminating silver*) may slowly precipitate, which may explode readily even in wet condition.

(4) Potassium iodide solution

Ag^+ ion reacts with I^- ion to form yellow precipitate of AgI, which is insoluble even in conc.NH_3 solution, but soluble in sodium thiosulfate solution due to the formation of dithiosulfatoargentate complex,



On boiling, the thiosulfato complex decomposes with change of colour from colourless $\rightarrow$ white $\rightarrow$ yellow $\rightarrow$ brown $\rightarrow$ black, due to precipitation of silver sulfide, Ag_2S .



To 2–3 drops of the aqueous or dil.HNO_3 solution of the sample in a semi-micro test tube add 1 drop of dil. KI ($\sim 10\%$) solution and shake. Yellow precipitate of AgI is immediately formed. Add 1 ml of water, shake and centrifuge. Reject the centrifugate with a capillary dropper. Add a few drops of sodium thiosulfate solution ($\sim 0.5\text{ M}$) to the precipitate and shake. If AgI is precipitated, it passes into solution. Even if a clear solution is not obtained, place the test tube with its contents in a hot water bath. White turbidity, gradually changing to yellow - brown and finally black, indicates Ag^+ .

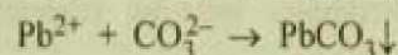
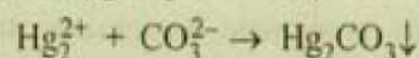
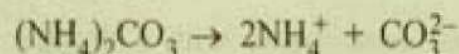
Confirmation

(1) Potassium chromate solution ($\sim 0.1\text{ M}$)

Ag^+ ion reacts with K_2CrO_4 solution producing red precipitate of silver chromate (Ag_2CrO_4), insoluble in dil.acetic acid , but soluble in dil.HNO_3



$\text{Hg}(\text{I})$ and $\text{Pb}(\text{II})$ ions give similar precipitates and interfere. These ions may be made unreactive by precipitation of their carbonates by treating the test solution with ammonium carbonate, which precipitates $\text{Hg}(\text{I})$ and $\text{Pb}(\text{II})$ as their carbonates but keeps $\text{Ag}(\text{I})$ in solution as the $[\text{Ag}(\text{NH}_3)_2]^+$ complex.



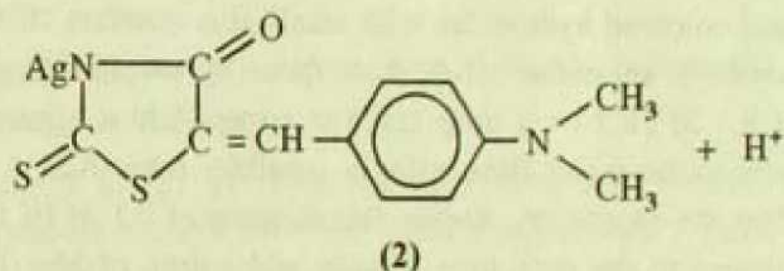
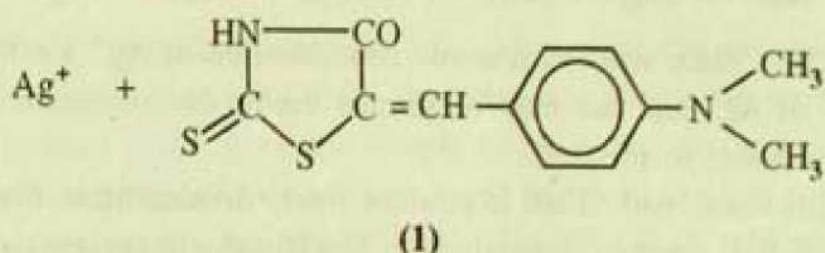
Tests for $\text{Ag}(\text{I})$ may be carried out in the clear solution obtained after separating the precipitated carbonates by centrifugation.

Place a drop of the test solution on a small watch glass or on a spot plate and add a drop of freshly prepared saturated ammonium carbonate solution and stir with a glass rod. If any precipitate is formed at this stage, remove one drop of the clear solution using a capillary dropper (place a small piece of cotton wool if necessary to facilitate separation of the solution from the precipitate). Place 1 drop of the clear solution on a drop-reaction paper and allow the spot to dry. Add a drop of K_2CrO_4 solution ($\sim 0.1 M$) at the centre of the spot. A red ring of silver chromate is formed if Ag^+ is present.

(2) *p*-Dimethylaminobenzylidene rhodanine (i.e. rhodanine reagent)

Reagent: 0.3% solution in acetone.

Ag^+ reacts with the rhodanine reagent (1) in weakly acidic solution to form a red-violet precipitate of $Ag(I)$ - rhodaninate complex (2).



Mercury, and copper (I) salts give similar compounds and so interfere.

Place a drop of the test solution on a drop-reaction paper and allow to dry. Add a drop of the rhodanine reagent and a few drops of dil.HCl or ammonium chloride. Mercury and $Cu(I)$ compounds with the reagent dissolve in the form of their sparingly dissociated chlorides or chloro complexes. The red-violet precipitate of $Ag(I)$ rhodaninate remains, as it is less soluble than $AgCl$.

Alternatively, the test with rhodanine reagent may be applied after removing these metal ions as carbonates by treating with ammonium carbonate solution as described before, in case of Ag_2CrO_4 precipitation. In this case the precipitated carbonates should be removed by centrifugation and the clear centrifugate is to be acidified with HNO_3 before applying the test.

Take 1-2 drops of the test solution in a centrifuge tube and add a few drops of freshly prepared saturated solution of ammonium carbonate. If a precipitate is formed, add sufficient ammonium carbonate solution to ensure complete precipitation. Centrifuge and transfer the clear centrifugate to a porcelain crucible with the help of a capillary dropper. Acidify with $2M HNO_3$ and evaporate to dryness inside a **Fume Chamber** to decompose the ammonium salts. Cool and take up the residue with 1-2 drops $2M HNO_3$. Place 1 drop of this solution on a spot

plate and then add 1 drop of the rhodanine reagent. A red-violet precipitate is formed if Ag^+ is present.

The test may also be carried out on a drop-reaction paper, when a red-violet stain is formed if Ag^+ is present.

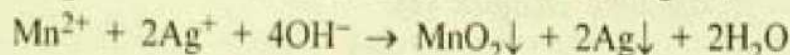
If no precipitate is formed on treatment of the test solution with ammonium carbonate, the test may be applied directly with the test solution in $2M \text{HNO}_3$.

Limit of identification: 0.02γ of Ag in $2M \text{HNO}_3$.

Limit of dilution: $1 : 2.5 \times 10^6$

(3) Test with Mn(II) nitrate (or sulfate) and alkali

On adding alkali to a mixture of Mn(II) and Ag(I) solution, a black precipitate consisting of a mixture of MnO_2 and metallic silver is formed according to,



The reaction takes place with such a low concentration of Ag^+ ion that even AgCl (i.e., the slight amount of Ag^+ ion that may be formed due to its ionization as $\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$ in water) responds to this test.

Mercury (I) salts reacts with alkali to produce finely divided black mercury. Hg(II) , Sn(II) and salts of noble metals react analogously with Mn(II) salts in presence of alkali. Metal ions forming insoluble and coloured hydroxides with alkali also interfere. If these interfering ions are present, it is advisable to isolate silver from these by precipitating as AgCl .

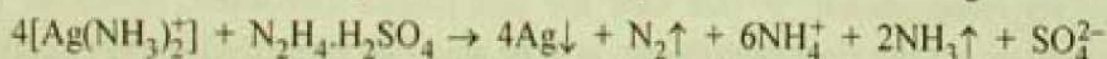
Place a drop of $0.1 M \text{HCl}$ on a drop reaction paper. Add a minute volume of the test solution at the centre of the moist flake using a capillary tube. Add a second drop of HCl on the paper and allow the spot to dry. Repeat this addition of $0.1 M \text{HCl}$ and the test solution 3 to 5 times and allowed to dry each time. Finally add a drop of Mn(II) nitrate (or sulfate) solution ($0.1 M$) and a drop of ($0.1 M$) NaOH solution. Immediate blackening occurs if Ag^+ is present.

Limit of identification: 2γ of Ag

Limit of dilution: $1 : 2.5 \times 10^4$

(4) Silver mirror test

When diammineargentate $[\text{Ag}(\text{NH}_3)_2]^+$ ion in solution is treated with hydrazine sulfate, the silver complex is reduced to form finely divided metallic silver, which deposits on the wall of the container, producing a shining silver mirror and hydrazine is oxidized to gaseous nitrogen.



Clean a semi-micro test tube with hot chromic acid solution, wash thoroughly with distilled water. Take 2 ml of the test solution and add dil.ammonia solution ($\sim 2M$) dropwise with shaking, until the precipitate of silver hydroxide that is initially formed, passes into solution completely. Then add 2 ml of hydrazine sulfate solution (saturated), mix uniformly. The silver mirror appears within a few seconds. Discard the solution immediately after the test (cf. p-236). Dissolve the silver mirror by washing with dil.HNO_3 ($\sim 8 M$).

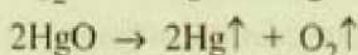
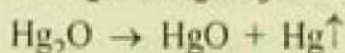
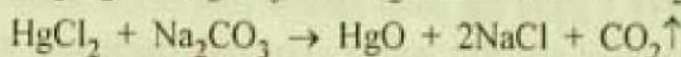
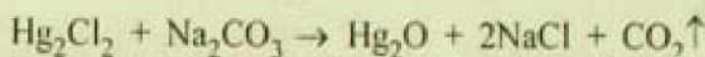


4.3 Reactions of Mercury (Hg^{I} & Hg^{II})

Indication

(1) Sublimate formation

Mercury compounds volatilize on heating in a dry test tube, but condense at the cooler upper part of the test tube forming a sublimate. Upon heating with a mixture of anhydrous Na_2CO_3 , mercury compounds irrespective of oxidation states of mercury, decompose to form metallic mercury, which forms shining mirror on the wall of the cooler part of the test tube.



Note: All mercury compounds, specially mercury vapour, are **extremely poisonous**. Only minute quantity (not more than ~ 0.1 g) of the substance should be used in the test.

Take a small amount (< 0.1 g) of the sample in clean and dry test tube. Plug the mouth of the test tube with a piece of clean cotton wool and hold the test tube slightly tilted on a small flame, and heat gently inside a **FUME CHAMBER**. A sublimate is formed at the cooler part of the test tube.

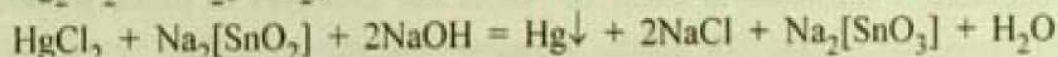
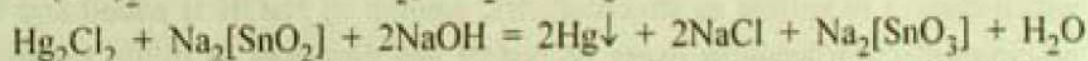
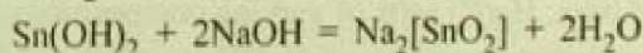
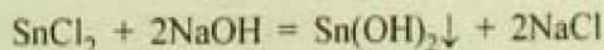
Caution: Don't inhale mercury vapour as it is **highly poisonous**.

(1a) If a sublimate is formed

Mix a small amount (> 0.1 g) of the sample with a large excess (7-8 times the bulk of the sample) of anhydrous Na_2CO_3 in a test tube, plugged with a piece of clean cotton wool and hold the test tube slightly tilted on a small flame inside a **FUME CHAMBER**. A grey mirror, consisting of globules of metallic mercury will be visible on the upper part of the test tube. The globules coalesce to form droplets of mercury, when rubbed with a glass rod.

(2) Sodium stannite solution

On treatment with a freshly prepared solution of sodium stannite, mercury compounds, irrespective of oxidation states of mercury, are reduced to finely divided black metallic mercury.



NB: Silver and bismuth compounds give similar tests with sodium stannite.

Sodium stannite solution may be prepared as follows:

Take 1 ml of stannous chloride solution (Notice that fine grains of metallic tin are visible at the bottom of the container) in a centrifuge tube. Add drops of NaOH solution (2 M) until the precipitate of $\text{Sn}(\text{OH})_2$ initially formed, dissolves in excess of the NaOH solution. Place

the centrifuge tube on a hot water bath for ~2 minutes and centrifuge. Use the clear centrifugate for the test.

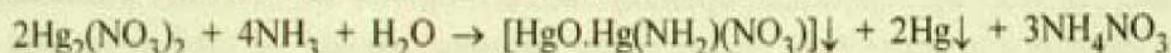
Place a minute quantity (<0.1 g) of the solid sample on a spot plate or a drop of the test solution on a drop-reaction paper. Add a drop of the freshly prepared sodium stannite solution. Immediate blackening occurs if mercury is present.

If the tests (1) and (2) are positive, one may proceed to confirmatory tests for Hg(I) or Hg(II), but still there are some more indicating tests.

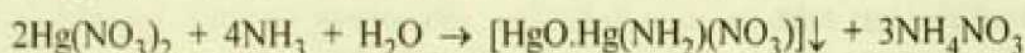
(3) Ammonia solution

Place a minute quantity (<0.1 g) of the solid sample (not black coloured) on a spot plate and add a drop of *aq*-NH₃ solution and stir with a glass rod. Immediate blackening indicates Hg(I).

In presence of aqueous ammonia, Hg(I) compounds disproportionate to form finely divided black metallic mercury (Hg⁰) and a aminomercuric (Hg^{II}) salt.



The test may also be conducted with an aqueous or dil.HNO₃ solution of the sample. If Hg(II) is present, instead of Hg(I), white precipitate of the aminomercuric salt is formed, which is soluble in large excess of ammonia and ammonium chloride.



The aminomercuric salt, HgO.Hg(NH₂)NO₃, also sublimes, like most mercury compounds.

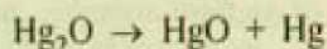
(4) Sodium hydroxide solution (~2M)

Hg(I):

Black precipitate of Hg(I) oxide, is formed



The precipitate is insoluble in excess NaOH, but soluble in dil.HNO₃. On boiling, the colour of the precipitate changes to grey as it disproportionates to HgO and Hg.



Hg(II):

Brownish-red precipitate of basic Hg(II) salts of varying compositions are initially formed, which change to yellow as stoichiometric amount of NaOH is added and HgO is formed. The precipitate is insoluble in excess of NaOH but dissolves in dilute mineral acids.



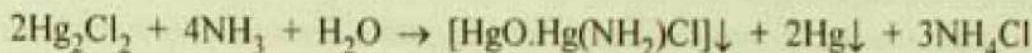
Hg(II) can be differentiated from Hg(I) by this reaction.

Place a drop of the test solution on a drop reaction paper and add a drop of NaOH solution (~2M) with a capillary dropper.

- A black spot indicates Hg(I),
- A yellow spot indicates Hg(II).

(5) Test with dil.HCl

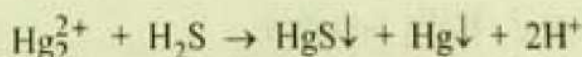
Forms a white precipitate of mercurous chloride (Hg_2Cl_2), insoluble in hot water [difference from Pb^{2+}], but turns black due to precipitation of Hg on treatment with *aq.* NH_3 solution [difference from Ag^+].



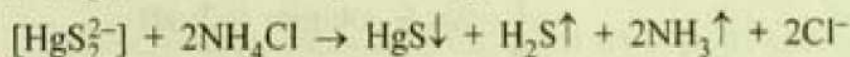
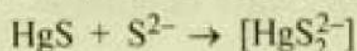
(6) H_2S - water and Na_2S solution (~2M)

Hg(I):

Due to extreme low solubility product of Hg(II) sulfide, HgS [$pK_{sp} = 53.6$], Hg(I) undergoes disproportionation when treated with H_2S -water, due to precipitation of black HgS and finely divided black metallic Hg.

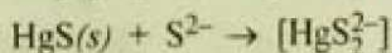
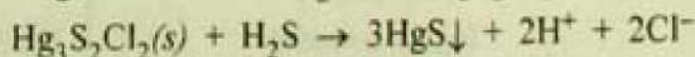
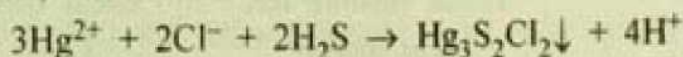


On treatment of the black mixture of HgS and Hg with sodium sulfide solution, HgS dissolves, forming disulfidomercurate (II), leaving metallic mercury. On removing the metallic mercury by centrifugation and treating the clear centrifugate with dilute mineral acid or with NH_4Cl , the black precipitate of HgS reappears.



Hg(II):

In presence of dil.HCl (~1M), H_2S reacts with Hg(II) salts, initially forming a white precipitate of Hg(II)-chlorosulfide ($\text{Hg}_3\text{S}_2\text{Cl}_2$), which then reacts with excess H_2S with change of colour from white to yellow to redish-yellow and finally forms black precipitate of HgS , insoluble in dil. HNO_3 , NaOH solution and ammonium sulfide solution, but soluble in sodium sulfide solution (2M) due to the formation of disulfomercurate (II) ion, $[\text{HgS}_2]^{2-}$:



The black precipitate of HgS reappears on treatment of the clear solution containing $[\text{HgS}_2]^{2-}$ ion with dilute mineral acids or with NH_4Cl .

(6a) Distinction between Hg(I) and Hg(II)

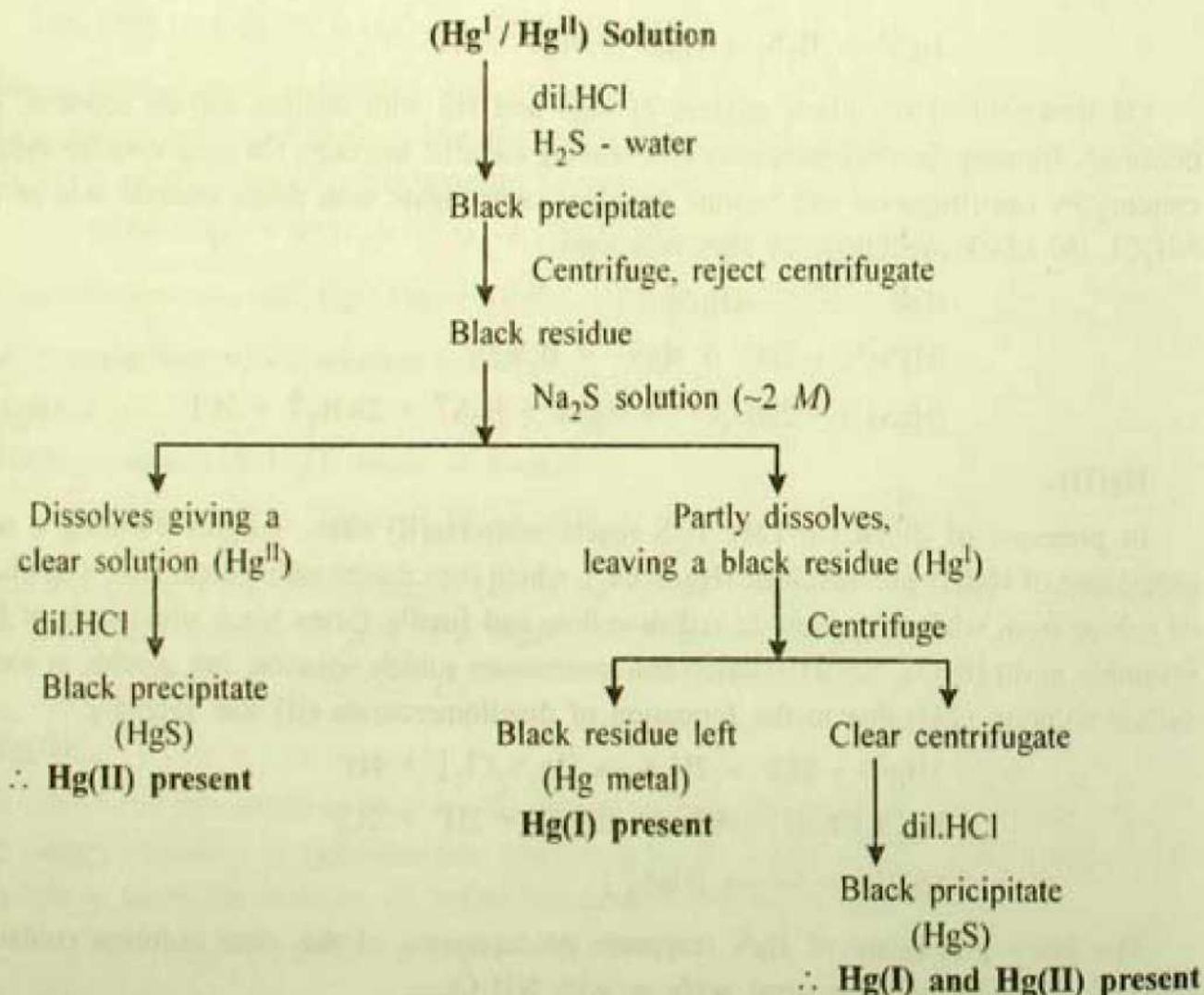
In case of Hg(I), the black precipitate obtained on treatment of the sample solution with H_2S -water consists of HgS and Hg metal. When this black precipitate is treated with Na_2S solution, HgS dissolves due to the formation of $[\text{HgS}_2]^{2-}$ ion, but black metallic Hg remains

undissolved. The centrifugate after separating from metallic Hg, on acidification, gives black precipitate of HgS.

In case of Hg(II), the black precipitate obtained on treatment of the test solution with H₂S-water contains only HgS, which dissolves in Na₂S giving a clear solution, which on acidification gives black precipitate of HgS.

Take 1 ml of the test solution on a semi-micro test tube and heat just to boiling. Add 1-drop of H₂S – water. If a precipitate is formed, add a few more drops of H₂S-water to complete the precipitation and then centrifuge. Reject the centrifugate. Treat the resulting black residue with 2 M Na₂S solution. If only Hg(II) is present, a clear solution of [HgS₂²⁻] results. Acidify with dil.HCl, black precipitate of HgS reappears. If Hg(I) is present, a part of the precipitate (HgS) dissolves, leaving a black residue (Hg). Remove the black residue by centrifugation. Acidify the centrifugate with dil.HCl. The black precipitate of HgS reappears.

The whole test is shown below schematically.

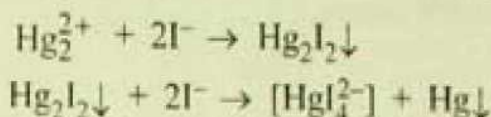


(7) Potassium iodide solution (10%)

Hg(I):

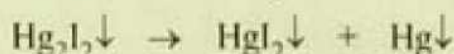
To 1-2 drops of the aqueous or dil.HNO₃ solution of the sample add 1 drop of KI solution. In presence of Hg(I) a green precipitate of mercurous iodide (Hg₂I₂) is first formed, which

reacts with excess of the reagent producing soluble tetraiodomercurate (II), $[\text{HgI}_4^{2-}]$ ion and black precipitate of finely divided metallic mercury, due to disproportionation:



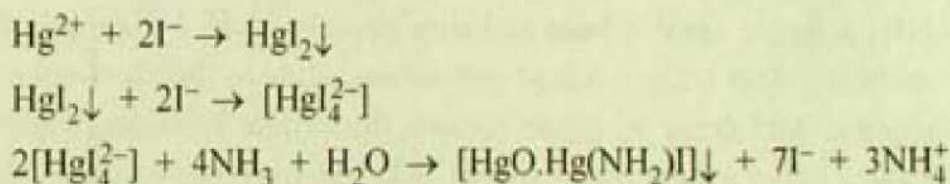
Remove the black residue of Hg by centrifugation. Place a drop of the clear centrifugate on a drop reaction paper, and hold the same over an open bottle of *aq*- NH_3 solution. A brown spot results.

Alternatively, instead of adding an excess of KI reagent, if the green precipitate of Hg_2I_2 is boiled with water, disproportionation still takes place, producing a mixture of red Hg(II) iodide (HgI_2) and black metallic Hg.



Hg(II):

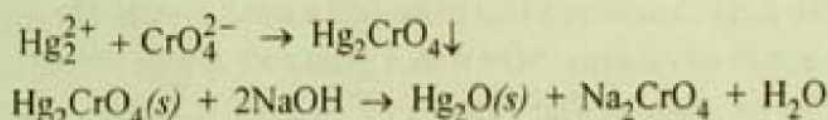
To 1-2 drops of the aqueous or dil. HNO_3 solution of the sample add 1 drop of KI solution. In presence of Hg(II), a red precipitate of HgI_2 is formed, which dissolves in excess of the reagent, producing tetraiodomercurate $[\text{HgI}_4^{2-}]$ ion, which turns brown on exposure to ammonia gas.



Place a drop of the clear solution containing $[\text{HgI}_4^{2-}]$ ion on a drop reaction paper using a capillary dropper and hold the paper over an open bottle of *aq*- NH_3 solution. The spot turns brown (*cf. Sect. 4.24, test of NH_4^+ ion with Nessler's reagent*).

(8) Potassium chromate solution

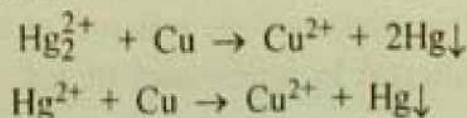
To 1-2 drop of the aqueous solution of the sample in a semi-micro test tube add 1 drop of K_2CrO_4 solution ($\sim 0.1M$). A brown amorphous precipitate of Hg(I) chromate of undefined composition is first formed, which changes to a red crystalline form on heating. On treatment with NaOH solution ($\sim 2M$) the red precipitate is transformed to black Hg_2O .



NB: Ag(I), Pb(II), Ba(II) also give similar tests with K_2CrO_4 solution.

(9) Polished copper sheet

Place a drop of the test solution on a polished red coloured copper sheet. A deposit of Hg metal is formed.

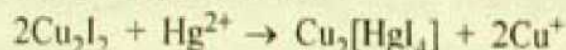


Rinse, dry and rub the spot with a piece of dry cotton wool, a glittery silvery spot will be visible. Heat the copper sheet on a Bunsen flame in side a *Fume Cupboard*. Hg evaporates and the red surface of copper becomes visible again.

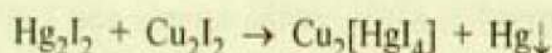
Confirmation

(1) Cuprous iodide slurry

Place a drop of cuprous iodide slurry on a spot paper and allow to dry. Add 1 drop of the weakly acidic test solution using a capillary dropper. A deep red to orange colouration depending upon the amount of mercurry developes, due to the formation of cuprous tetraiodomercurate, $\text{Cu}_2[\text{HgI}_4]$ complex,



With Hg(I) , the following reactions may take place:



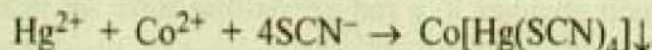
Preparation of Cu_2I_2 slurry

Take 1 ml of 5% copper sulfate solution in 1M HCl in a centrifuge tube, add drops of dil.(1:1) aq- NH_3 solution until a faint turbidity appears. Add 1-2 drops of dil.acetic acid to dissolve the turbidity. Add 1-2 crystals of potassium iodide to the clear solution, when a brown precipitate appears. Add drops of dilute sodium thiosulfate solution, when the brown colour is discharged and a milky white precipitate of Cu_2I_2 become clearly visible. Wash the precipitate with water by centrifugation and preserve the slurry in corked bottle.

Limit of identification: $\sim 3 \times 10^{-3} \gamma$ of Hg (in ~ 0.03 ml).

(2) Co (II) acetate-Ammonium thiocyanate test or Cobalt-mercurothiocyanate test

Hg (II) salts react with concentrated solution of Co(II) acetate in presence of a small amount of ammonium thiocyanate, producing a deep-blue crystalline precipitate of Co(II) mercurothiocyanate, or cobalt tetrathiocyanatomercurate (II), $\text{Co}[\text{Hg}(\text{SCN})_4]$.



Place a drop of the test solution on a spot plate, add a small crystal of ammonium thiocyanate and a grain of solid cobalt (II) acetate. Stirr with a glass rod. A blue colour or a blue crystalline precipitate appears in presence of Hg^{2+} ions.

(3) Decomposition of ferrocyanide ion

Reagent: (i) 0.2% $\text{K}_4[\text{Fe}(\text{CN})_6]$ in 0.01M HNO_3

(ii) 0.005 M 1,10-phenanthroline in 0.01 M HNO_3 .

Due to greater softness as a Lewis acid, Hg^{2+} ion snatches the soft CN^- ion from ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}$ complex and sets free comparatively less soft or borderline Fe^{2+} ion in solution. The presence of Fe^{2+} ion is indicated by appearance of red colouration if 1-10

phenanthroline (phen) or 2, 2'-bipyridine (bipy) is also present in the reaction mixture. Hg(II) should be present as its nitrate or sulfate salt. The test is unsatisfactory with HgCl₂ solution. Ag⁺ ion gives similar reaction, and should be removed by precipitation as AgCl. Before applying this test, Hg(II) should be precipitated as HgO by treating the test solution with NaOH solution (~1 M) and washed free from Cl⁻ ion by repeated centrifugation and washing with water. The Cl⁻ free HgO should be dissolved in minimum amount of dil.HNO₃ (~0.1M). The solution should be diluted to adjust 0.01 M acidity before applying this test.

Place 1 ml of 0.005 M 1,10-phenanthroline and 1-2 drops of 0.2% K₄[Fe(CN)₆] solution in a semi-micro test tube and add, 1 drop of the sample solution. Shake and place the test tube in a hot water bath for 1 minute. Red colouration appears in presence of Hg²⁺ ions.

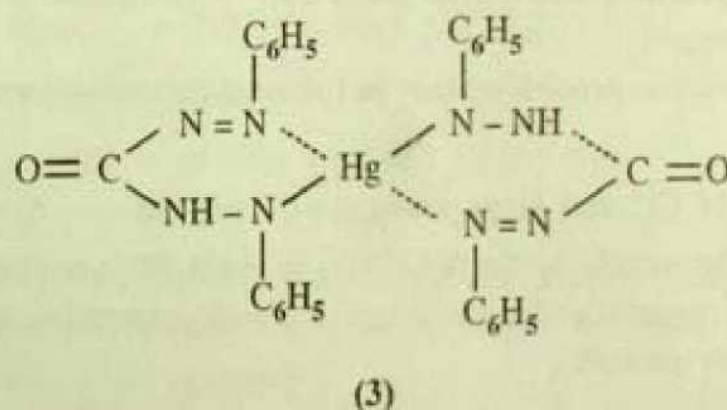
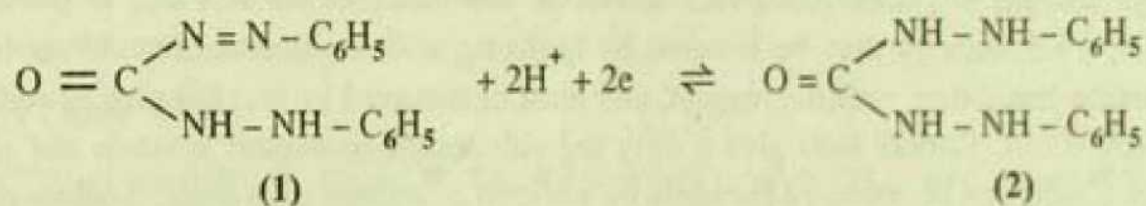
Limit of identification: 2γ of Hg

Limit of dilution: 1:20 × 10⁶

(4) 1, 5-Diphenylcarbazone

Reagent: 1% alcoholic solution of diphenylcarbozone.

Both diphenylcarbazone (1) and its reduction product, diphenylcarbazide (2) react with mercury salts to produce blue to violet insoluble precipitate of inner metallic complexes. The structure of the complex of Hg(II) with (1) is shown below (3). The Hg(I) complex maybe formulated accordingly.



Sensitivity of the reaction is lowered with increase of acidity of the test solution. Heavy metals (Fe, Co, Cu and others) also form coloured precipitate with diphenylcarbazone. However, in 0.2 M HNO₃ medium this reaction with diphenylcarbazone is specific for mercury. Chromate and molybdate also form coloured compounds with both diphenylcarbazone and diphenylcarbazide. Interference due to chromate is eliminated by reducing it to nonreacting Cr(III) salts by treating the test solution with H₂O₂ or SO₂- water. Interference due to molybdate may be eliminated by masking it with oxalic acid, since the oxalato-molybdate complex does not react with the reagent.

Mix a drop of the freshly prepared 1% alcoholic solution of the reagent and a drop of 0.2 M HNO_3 on a small watch glass or on a spot plate. Place a drop of this mixture on a drop-reaction paper and allow the spot to dry. Add a drop of the test solution on the spot using a capillary dropper. Depending upon the concentration of mercury, a violet to blue fleck appears.

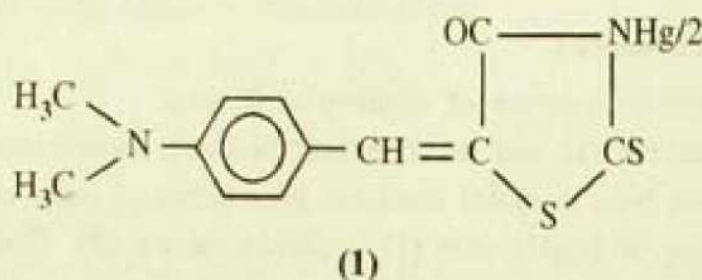
Identification limit : 0.1 ~ 1.0 γ of Hg

Dilution limit : 1 : (0.5 ~ 5) $\times 10^6$

(5) *p*-Dimethylaminobenzylidene rhodanine

Reagent: Saturated solution in ethanol.

In weakly acidic solution, mercury salts give a red-violet precipitate (1) with an alcoholic or acetone solution of the reagent, *p*-dimethylaminobenzylidene rhodanine (or, *rhodanine reagent*).



Large amount of chloride and HCl lower the sensitivity of the test due to the formation of $[\text{HgCl}_4]^{2-}$ ion. Acidity may be lowered by buffering with sodium acetate. Silver (Ag^+) ion gives similar precipitate with the reagent, and must be removed by precipitating as AgCl before applying this test. Copper salts give a dirty red colouration in neutral solution and should be removed. Cu(II) can be rendered harmless by addition of sodium phosphate. Sodium phosphate increases the *pH* and precipitates Cu(II) as green Cu(II) - phosphate, which reacts very slowly with the rhodanine reagent.

The following alternative procedures may be followed for testing for mercury with rhodanine reagent.

(5a) In absence of Cl^- and large amount of free acid

Place a drop of the weakly acidic (dil.HNO_3 or $\text{dil.H}_2\text{SO}_4$) test solution on a spot plate and add 1 drop of the reagent. Violet precipitate or a pink colouration appears depending upon the amount of mercury present.

(5b) In presence of Cl^- and free acid

Place a drop of sodium acetate plus a drop of the reagent in two adjacent cavities of a spot plate. Yellow to orange colouration is produced in both the cavities. Add a drop of the test solution on one of the cavities, a pink colouration is produced if mercury is present. Compare with the blank, which is orange-yellow.

(5c) In presence of copper

Place 1 drop of the test solution on a spot plate, add 5 drops of 10% sodium phosphate solution and stir with a glass rod. A green precipitate is formed if copper is present. Add

1 drop of rhodanine reagent. A violet to pink colouration is produced if mercury is present. Run a blank test if very small amount of mercury is suspected.

Limit of identification: 0.33γ of Hg

Limit of dilution: 1 : 1.5×10^5

4.4 Reactions of Lead (Pb^{II})

Indication

Tests on the solid sample

- (i) **Dry test tube heating:** White sample: turns yellow when hot and cold.
- (ii) White sample: turns black on treatment with H_2S -water.
- (iii) White sample : turns yellow-orange on treatment with potassium chromate solution.
- (iv) White sample: turns golden yellow on treatment with KI solution.
- (v) Black sample: turns white on treatment with H_2O_2 .

Wet reactions

The following tests may be performed with aqueous or HNO_3 extract of the sample. If Ba^{2+} , Sr^{2+} , Ca^{2+} are suspected, sodium hydroxide extract (contains sodium plumbite, $\text{Na}_2[\text{PbO}_2]$) may be used after neutralization with dil. HNO_3 .

Take 1-2 drops of the test solution in a semi-micro test tube and add 1-2 drops of the following reagents and proceed accordingly.

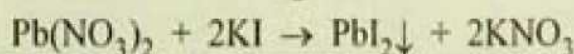
(1) Dilute HCl

White precipitate of PbCl_2 in the cold, soluble on boiling, but reappears on cooling (difference from Hg_2Cl_2 and AgCl):

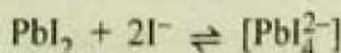


(2) Potassium iodide solution

Golden yellow precipitate of PbI_2 appears,

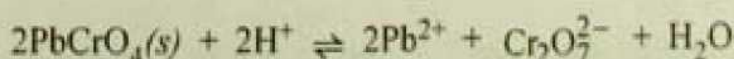


The precipitate almost dissolves on boiling, but reappears on cooling. The precipitate dissolves in excess of the reagent due to the formation tetraiodoplumbate(II) complex:



(3) Potassium chromate in neutral, acetic acid or in ammoniacal solution

Yellow precipitate of PbCrO_4 is formed. The precipitate is soluble in dil. HNO_3 and also in NaOH solution:



(4) Dilute H_2SO_4 (or, soluble sulfate solution)

To 1 ml of the test solution in a semi-micro test tube add 1 ml of ethanol and a few drops of dil. H_2SO_4 (or a solution of $\text{Na}_2\text{SO}_4/\text{K}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$). Heavy white precipitate of PbSO_4 comes down.

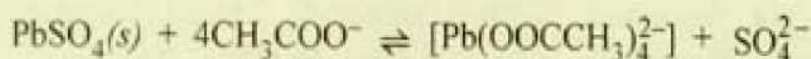


Centrifuge and reject the centrifugate. Wash the precipitated PbSO_4 with water twice by centrifugation and divide the residue in to 4 parts, transfer each part to separate semi-micro test tubes and perform the following tests:

4(a) Part (i): Add 2-3 drops of conc. H_2SO_4 to the precipitated PbSO_4 and boil for 1-2 minutes. The precipitate passes into solution due to the formation of lead hydrogen sulfate:



4(b). Part (ii): Add 1-2 ml of ammonium acetate solution (6M) and boil for 1-2 minutes. The precipitate of PbSO_4 passes into solution due to the formation of tetraacetatoplumbate (II) complex:



Add 1 ml of potassium chromate to the clear solution. Yellow precipitate of lead chromate is formed,



4(c). Part (iii): Add 1-2 ml of ammonium tartarate $[(\text{NH}_4)_2 \text{C}_4\text{H}_4\text{O}_6]$ solution (6M) and boil for 1-2 minutes. The precipitate of PbSO_4 passes into solution due to the formation of ditartaratoplumbate (II) complex:



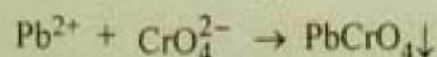
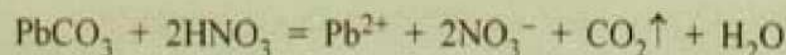
Add 1 ml of potassium chromate reagent to the clear solution. Yellow precipitate of lead chromate appears:



4(d) Part (iv): Add 1-2 ml of sodium carbonate and boil for some time. PbSO_4 is transformed to PbCO_3 by double displacement, or, precipitate-exchange reaction,

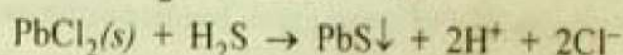


Centrifuge and wash the residue repeatedly with water by centrifugation to remove SO_4^{2-} ion. Dissolve the washed precipitate of PbCO_3 in dil. HNO_3 add a few drops of saturated sodium acetate solution followed by 1 ml of K_2CrO_4 solution. Yellow precipitate of PbCrO_4 appears.

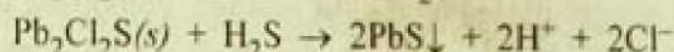
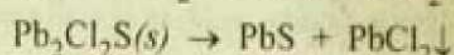
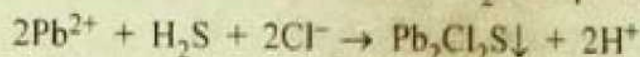


(5) H₂S-water

In neutral or weakly acidic solution (< 2M) Pb²⁺ reacts with H₂S to form black precipitate of PbS. Precipitated PbCl₂ is also transformed into PbS by precipitate-exchange reaction:



In presence of large amount of chloride, initially a red precipitate of lead chlorosulfide (Pb₂Cl₂S) is formed, which reacts with excess H₂S to produce black precipitate of PbS.



H⁺ ions liberated in these reactions suppress the concentration of S²⁻ ion by common ion effect. Appreciable concentration of S²⁻ ion may be achieved by performing the test in presence of sodium acetate, which acts as a buffer (CH₃COO⁻ + H⁺ ⇌ CH₃COOH).

When the precipitated black PbS is boiled with H₂O₂ (3%), it is oxidised to white PbSO₄



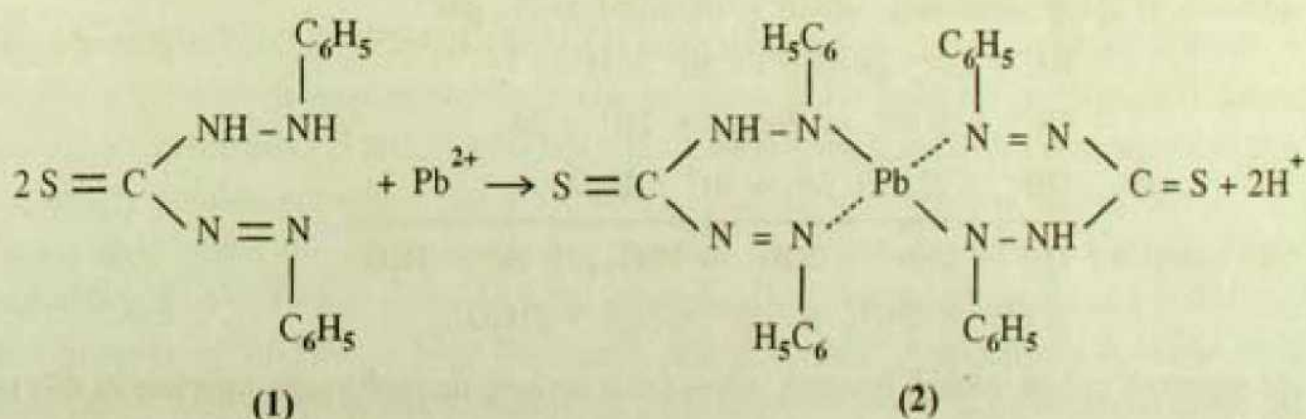
Wash the precipitate of PbS with water by repeated centrifugation, discard the centrifugate and the washings. Treat the black PbS with a few drops of H₂O₂ and warm on a hot water bath. The black colour changes to white (PbSO₄).

Confirmation

(1) Test with diphenylthiocarbazone (Dithizone)

Reagent: ~ 1-2 mg of dithizone in 100 ml of CCl₄.

Dithizone (1) reacts with Pb²⁺ in neutral solution to give a red precipitate of the inner metallic complex (2)



The solution of dithizone reagent in CCl₄ has a green colour. Pb(II) - dithizonate complex (2) is red coloured and is soluble in CCl₄ and other non-polar organic solvents. As a result, the green colour of the reagent solution in CCl₄ becomes red in presence of Pb²⁺.

Many other metal ions also form coloured dithizonate complexes which are also soluble in organic solvents. But their interference can be eliminated by complexing them with alkali

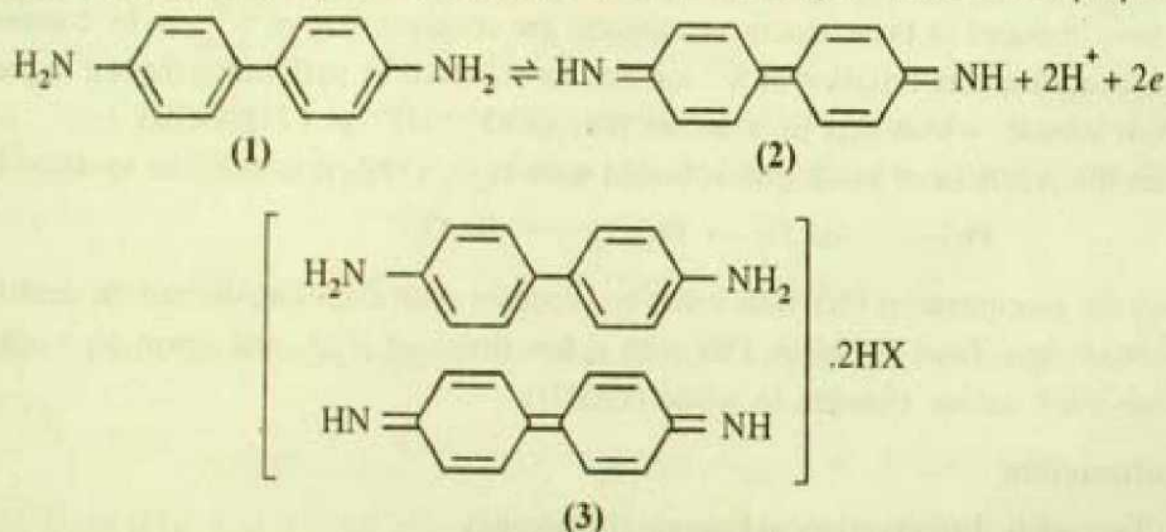
tartarate solution. The dithizone reagent is so specific for Pb^{2+} that even tartarate that masks other metal ions, can not mask Pb^{2+} in presence of this reagent.

Take a drop of the test solution in a semi-micro test tube and add 1-2 drops of sodium-potasium tartarate solution ($\sim 0.1M$) and an equal volume of the CCl_4 solution of dithizone. Shake the mixture vigorously. In presence of Pb^{2+} , the green reagent solution assumes a brick-red colouration, which is easily visible against a white back ground.

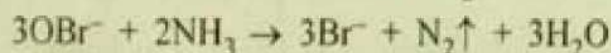
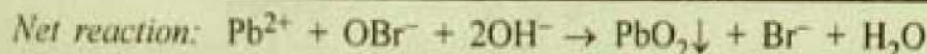
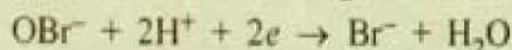
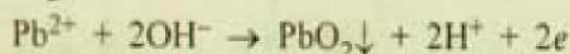
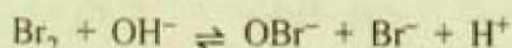
(2) Test with benzidine

Reagent: 0.05% solution of benzidine in 10% acetic acid.

Lead dioxide (PbO_2) and many other oxidizing agents oxidize the diamine, benzidine (1) to benzidine blue (3), which is a meriquinoid oxidation product, composed of the diamine (1), the dimine (2) and a monoprotic acid (HX, here, acetic acid) in 1:1:2 molar proportion.



Pb(II) compounds may be oxidized to PbO_2 by hypobromite (OBr^-) ion generated *in situ* by the reaction of bromine water and alkali. Hypobromite ion is considered as the most suitable oxidant for this reaction as because the excess hypobromite, if there be any, may be decomposed by addition of dilute ammonia, which is oxidized to N_2 gas.



Manganese, cobalt, nickel, bismuth, silver (also cerium, thorium) salts interfere in this test. But these may be rendered harmless by conducting the test with alkali (NaOH) extract of the sample, which contains lead as plumbite, Pb(OH)_2^{2-} ion, (only thorium* interferes under this condition). Other metal ions are precipitated as their hydroxides/oxides. Bismuth salts are precipitated as BiO(OH) , which is not oxidized by hypobromite.

*Rare element

Place a drop of the 3M NaOH extract of the sample on a drop reaction paper, add 1 drop of saturated Br₂ - water and allow the spot to dry. Add 2 drops of 1:1 aqueous - NH₃ and allow to spread. Remove the excess NH₃ by holding the paper near a small flame or over a watch glass covering a beaker of boiling water. Add 1 drop of benzidine reagent in acetic acid. Depending upon the amount of lead present, a light blue to deep blue fleck is formed on the paper. If very small amount of Pb²⁺ is present, the blue colour gradually fades away. Run a blank test.

Alternatively, take 1 ml of the test solution in a semi-micro test tube and treat it with 3 ml of 3M NaOH solution and 2 ml of saturated Br₂-water. Boil for a few minutes and filter through a Whatman No. 1 filter paper. Wash the residue on the filter paper with (1:1) aqueous - NH₃ followed by hot water to remove excess BrO⁻ ion. Add 1 drop of acetic acid solution of benzidine on the filter paper. A blue colouration is produced if lead is present.

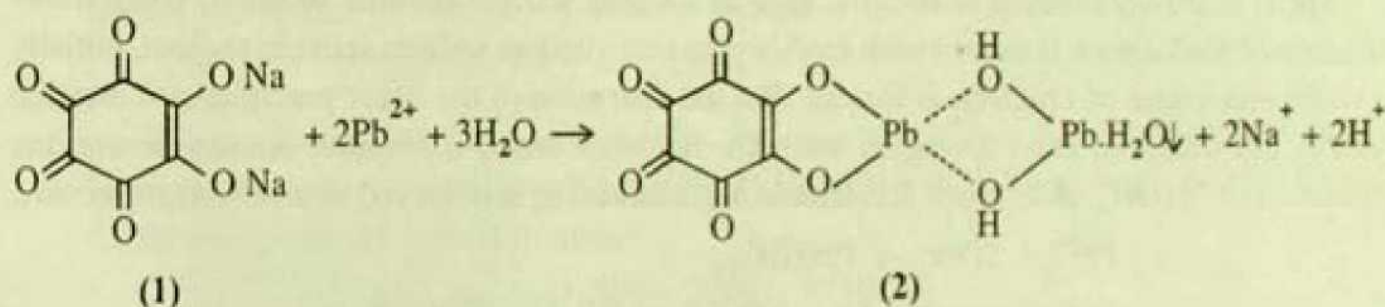
Limit of identification: 1γ of Pb *Limit of dilution* : 1 : 5 × 10⁴

(3) Test with sodium rhodizonate

Reagent: (i) 0.2% solution of sodium rhodizonate in water.

(ii) Bufler solution (pH = 2.8) : 1.9 g of sodium hydrogen tartarate and 1.5 g of tartaric acid in 100 ml of water.

When sodium rhodizonate (1) reacts with neutral or weakly acidic solution of Pb²⁺ salts, coloured precipitate of basic lead rhodizonate (2) is formed.



The precipitate Pb(C₆O₆).Pb(OH)₂.H₂O (2) that is formed in neutral solution is violet in colour. The precipitate formed in weakly acidic solutions of Pb²⁺ salts is scarlet-red in colour and has the stoichiometry, 2Pb(C₆O₆).Pb(OH)₂.H₂O. Both these reactions are so sensitive that even sparingly soluble materials, like PbS, PbSO₄, PbCrO₄ etc. respond to this test.

Place a drop of the test solution on a drop reaction paper and allow the spot to dry. Touch the spot with a drop of freshly prepared 0.2% solution of sodium rhodizonate using a capillary dropper. In presence of Pb²⁺, a blue fleck or a ring is formed. If an intense colouration is produced, add 1 drop of the buffer solution (pH 2.8). The blue colour is transformed to scarlet red colour.

Limit of identification : 0.1γ of Pb

Limit of dilution : 1 : 5 × 10⁵

4.5 Reactions of Bismuth (Bi^{III} , Bi^{V})

Indication

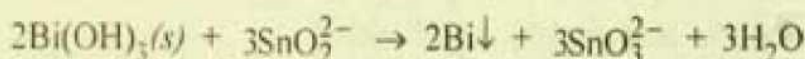
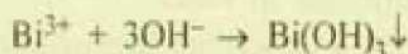
(1) Blackening with sodium stannite

Reagent: Freshly prepared $\sim 0.125M$ sodium stannite.

Take 2 ml of stannous chloride ($\sim 0.25M$) in a centrifuge tube and add drops of $2M$ NaOH solution, until the white precipitate initially formed, is dissolved in excess of NaOH solution. Warm the solution gently and centrifuge, use the clear centrifugate for the tests. The reagent does not keep, always freshly prepared solution is to be used.

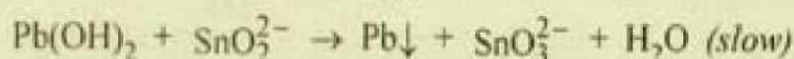
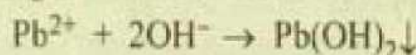
Take a grain of the solid sample or a drop of the test solution on a spot plate and add 1 drop of the freshly prepared sodium stannite solution. Immediate blackening takes place if bismuth is present.

Initially Bi^{3+} reacts with NaOH present in the reagent to produce white precipitate of bismuth hydroxide, which is reduced by sodium stannite to finely divided black metallic bismuth.

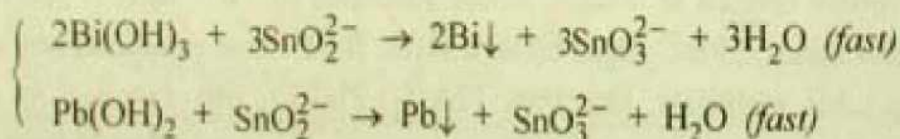


(2) Test by induced reduction of Pb(II)

Pb(II) is slowly reduced to metallic lead by alkaline sodium stannite solution. When dilute solution of lead nitrate is treated with freshly prepared alkaline sodium stannite reagent, initially a white precipitate of $\text{Pb}(\text{OH})_2$ is formed. But the formation of the black precipitate of metallic lead is not observed even during an hour. On the other hand, if bismuth is also present, the reduction of $\text{Pb}(\text{OH})_2$ is so much accelerated that blackening is observed almost instantaneously.



But,



Reduction of $\text{Bi}(\text{OH})_3$ induces the reduction of $\text{Pb}(\text{OH})_2$. Induced reactions like this, are different from catalytic reactions. In an *induced reaction*, the inducer (here, $\text{Bi}(\text{OH})_3$) is itself used up and not regenerated. In a *catalytic reaction*, the catalyst is regenerated, not used up.

N.B. Silver, mercury, copper interfere in this reaction. $\text{Cu}(\text{II})$ may be rendered harmless by complexation with tartarate.

Limit of identification: 0.01γ Bi

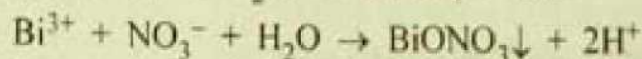
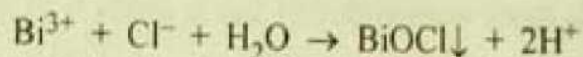
Limit of dilution : $1 : 5 \times 10^6$

Place 1 drop of $0.25 M$ lead nitrate solution on two adjacent cavities of a spot plate and add one drop of freshly prepared sodium stannite in each cavity. Add one drop of the test

solution in one of the cavities and one drop of distilled water in the other. Immediate blackening is observed if the test solution contains bismuth.

(3) Oxy salt formation

Pour 1-2 drops of dil.HCl or dil.HNO₃ extract of the sample into a large volume of water in a test tube or in a small beaker. Milky white precipitate appears due to oxy salt formation if bismuth is present.



Centrifuge and divide the precipitate into three parts in three semi-micro test tubes.

3(a): Part-I : Add dil.HCl, or dil.HNO₃. The precipitate dissolves if it is BiOCl or BiONO₃.

3(b): Part-II : Treat the precipitate with NaOH solution (~2M). Precipitate does not dissolve, (distinction from tin).

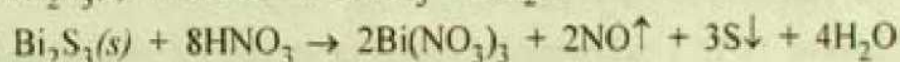
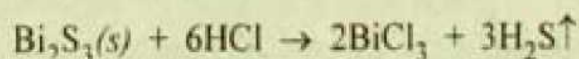
3(c): Part-III: Treat the precipitate with tartaric acid. Precipitate does not dissolve, (distinction from antimony)

(4) H₂S - water

To 1-2 drops of the test solution in a semi-micro test tube add 1-2 drops of H₂S-water. Brown precipitate of bismuth sulfide is formed.

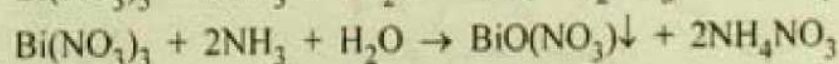
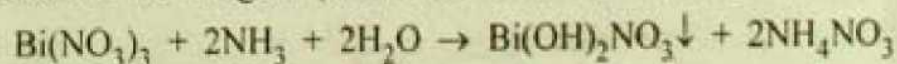


The precipitate does not dissolve in dil. hydrochloric acid or in ammonium sulfide solution. However, it dissolves in boiling conc.HCl with liberation of H₂S and in hot dil.HNO₃ producing white precipitate of colloidal sulfur.



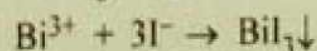
(5) Aqueous – NH₃ solution

To 1-2 drops of the test solution in a semi-micro test tube add drops of (1:1) aqueous – NH₃. White precipitate of basic bismuth salt of varying composition is produced, which does not dissolve in excess of the reagent (difference from Cu²⁺ and Cd²⁺).

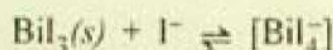


(6) Potassium iodide solution

To 1-2 ml of dil.HCl or dil.HNO₃ solution of the sample add 1 drop of 10% KI solution. Black precipitate of BiI₃ is produced if bismuth is present.

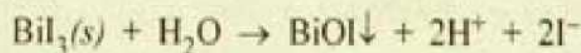


Add a few more drops of the KI reagent to the black precipitate and shake. The precipitate dissolves producing an orange coloured solution due to the formation of tetraiodobismuthate (III):



Dilute the resulting solution by pouring it into a large volume of water in a test tube or in a small beaker, the reverse reaction takes place and black precipitate of BiI_3 reappears.

Boil the precipitate with water, it turns orange due to the formation of bismuth oxyiodide (or bismuthyl iodide):

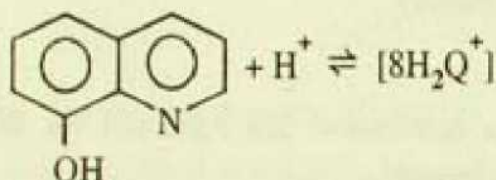


Identification limit : 25γ of Bi.

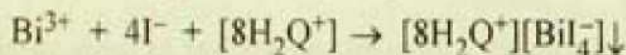
Confirmation

(1) 8-Hydroxyquinoline (5%) - KI (6M) reagent

Place a drop of the reagent on a drop-reaction paper and allow the spot to dry. Add 1 drop of weakly acidic test solution on the spot using a capillary dropper. A red spot appears due to the formation of 8-hydroxyquinoline-tetraiodobismuthate complex.



8-Hydroxyquinoline (8HQ)



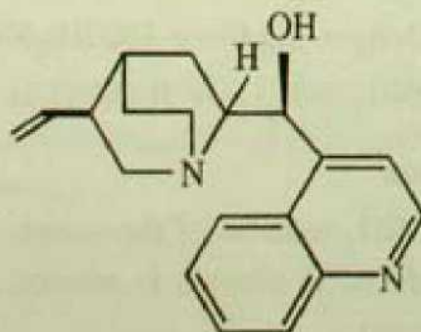
In the absence of other halide ions, this reaction is characteristic for Bi^{3+} ion.

Identification limit: 1γ of Bi.

(2) Test with cinchonine-KI reagent

Reagent: Dissolve 1g of cinchonine by warming in 100 ml of distilled water containing a few drops of HNO_3 . Cool the solution to room temperature and dissolve 2g of KI in it.

In presence of KI, cinchonine base (**B**) reacts with weakly acidic solution of bismuth (III) salts to produce orange-red precipitate of double iodide of formula, $\text{BiI}_3 \cdot \text{B} \cdot \text{HI}$, which may be regarded as the cinchoninium salt, $\text{BH}^+[\text{BiI}_4^-]$, of iodobismuthic acid, $\text{H}[\text{BiI}_4]$.



[B] Cinchonine

Place a drop of the reagent on a drop reaction paper and allow the spot to dry. Add a drop of the weakly acidic test solution on the spot using a capillary dropper. Appearance of orange-red fleck indicates Bi^{3+} ion.

Identification limit: 0.15γ of Bi.

Dilution limit : 1 : 3.5×10^5

(2a) Test for Bi^{3+} in presence of other metal ions

Pb^{2+} and Hg^{2+} form coloured iodide salts. Cu^{2+} oxidizes iodide to liberate iodine with precipitation of Cu_2I_2 , which appears as a brown precipitate in presence of iodine. Thus, Cu^{2+} , Pb^{2+} and Hg^{2+} interfere the cinchonine - KI test for Bi^{3+} . Within certain limitations, however, the test for Bi^{3+} can be carried out even in the presence of these interfering ions, since due to different rates of diffusion of these ions through the capillaries of the drop reaction paper (Whatman No. 1 filter paper), they are concentrated at different zones of the paper. Moreover, Cu^{2+} , Pb^{2+} and Hg^{2+} ions react with I^- ion present in the reagent solution at different rates. Thus, when a drop of the weakly acidic (dil. HNO_3) test solution containing Bi^{3+} , Cu^{2+} , Hg^{2+} and Pb^{2+} ions is placed on the drop reaction paper impregnated with the cinchonine-KI reagent, four different zones can be observed:

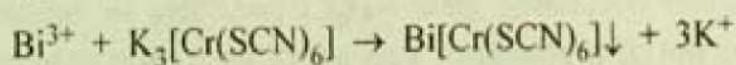
- (1) : a white central ring containing the mercury compound,
- (2) : an orange coloured ring containing the bismuth compound,
- (3) : a yellow ring of lead iodide,
- (4) : a brown ring of iodine liberated by the reaction Cu(II) with KI.

The rings or the zones will be wider or narrower depending upon the concentrations of the different metal ions.

(3) Test with potassium chromithiocyanate, $\text{K}_3[\text{Cr}(\text{SCN})_6]$, reagent

Reagent : 3% Alcoholic solution of $\text{K}_3[\text{Cr}(\text{SCN})_6]$.

In weakly acidic solution Bi(III) salts react with $\text{K}_3[\text{Cr}(\text{SCN})_6]$ complex producing an insoluble brick-red precipitate of bismuthchromithiocyanate:



Hg^{2+} , Ag^+ , Tl^+ and Pb^{2+} also give insoluble products with this reagent, but the colour of these products are either yellow or pink.

Place a micro drop of the test solution on a drop-reaction paper with the help of a capillary tube and allow the paper to dry by placing it on a watch glass covering a beaker of boiling water. Add 1 drop of alcoholic solution of the reagent and dry as before. Add 1-2 drops of $\text{dil. H}_2\text{SO}_4$ using a capillary dropper. A brick-red fleck or ring is produced depending upon the bismuth content.

Limit of identification: 0.4γ of Bi.

Limit of dilution : 1 : 3.1×10^4



4.6 Reactions of Copper (Cu^I & Cu^{II})

Indication

(1) Flame test

Green flame in presence of halides, i.e., when the sample is moistened with conc.HCl.

(2) Borax-bead test

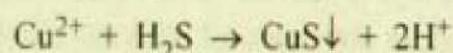
Oxidizing flame: green when hot, blue when cold.

Reducing flame: Colourless or opaque red.

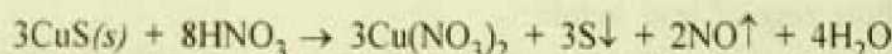
(3) H_2S -water or ZnS slurry

The test may be applied directly on the solid sample if it is not black coloured. Otherwise the test may be applied on aqueous or weakly acidic solution of the sample.

Place a drop of the test solution or a grain of the solid sample (if not black) on a spot plate and add 1 drop of H_2S - water. Immediately black precipitate of CuS appears.



The precipitate is insoluble in dil. H_2SO_4 (~ 1M) even on boiling (distinction from CdS), insoluble in Na_2S solution (distinction from HgS), NaOH and ammonium sulfide solutions, but soluble in hot.dil. HNO_3 with separation of sulfur.



Alternatively, place a drop of the test solution on a spot paper and add a drop of H_2S -water. A black spot results due to the formation of CuS .

The test may also be conducted with a slurry of zinc sulfide, which may be prepared as follows:

Take 1 ml of zinc acetate solution (1%) in 2% NH_4Cl in a centrifuge tube, add a few drops of *aq*- NH_3 solution to render the solution ammoniacal. Add drops of H_2S -water, when white precipitate of ZnS appears. Centrifuge and reject the centrifugate. Wash the white precipitate of ZnS with water containing little NH_4Cl and NH_3 by repeated centrifugation.

Now place a small amount of precipitated ZnS slurry on a drop reaction paper and allow the spot to dry. Place a drop of the test solution on the white spot of ZnS . Immediate blackening will be observed if Cu^{2+} is present.



The above reaction proceeds from left to right as the solubility product of CuS is much lower than that of ZnS .

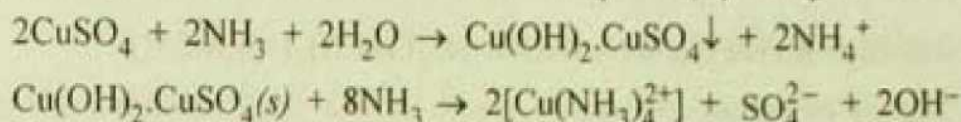


All metallic sulfides of solubility product lower than that of ZnS respond to this test. Interference due to CdS (yellow) can be eliminated by adjusting the acidity to ~0.3 M. However,

mercury, lead, bismuth interfere. Co^{2+} , Ni^{2+} , Mn^{2+} may be rendered harmless by conducting the test in acid ($\sim 0.3M$) medium.

(4) Ammonia solution

To 1 drop of neutral or weakly acidic test solution add 1 drop of dilute aq-NH_3 solution. Sky blue precipitate of basic copper salt appears, which dissolves on addition of excess of ammonia, forming a deep blue solution of tetraamminecuprate (II) complex ion :



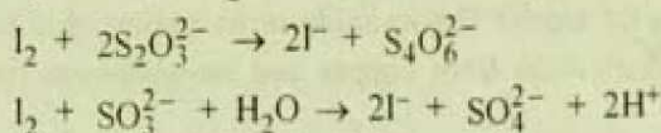
This reaction is characteristic of Cu^{2+} in absence of Ni^{2+} . The test may even be applied on solid copper compounds except CuS .

(5) Potassium iodide (10%) solution

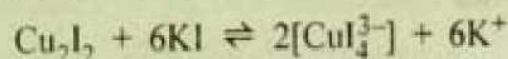
Although $E^\circ(\text{Cu}^{2+}/\text{Cu}^+)$, +0.153 volt is less than $E^\circ(\text{I}_2/2\text{I}^-)$, +0.54 volt, but due to lower solubility of cuprous iodide (Cu_2I_2 , $pK_{sp} = 11.96$), the formal potential (E') of $\text{Cu}^{2+}/\text{Cu}^+$ couple exceeds that of $\text{I}_2/2\text{I}^-$ couple in presence of I^- ions. As a result, Cu^{2+} oxidizes I^- to liberate I_2 with precipitation of Cu_2I_2 , (cf. Sect. 2.4).



Although Cu_2I_2 is milky white, but due to adsorption of I_2 on it, the resulting precipitate appears brown in colour, which on addition of drops of sodium thiosulfate, or, sodium sulfite solution, turns milky white, as I_2 is reduced to I^- by these reagents,

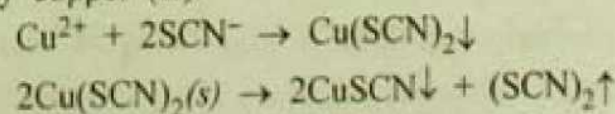


The precipitate of Cu_2I_2 dissolves in excess of KI solution due to the formation of the complex, $[\text{CuI}_4]^{3-}$ ion :

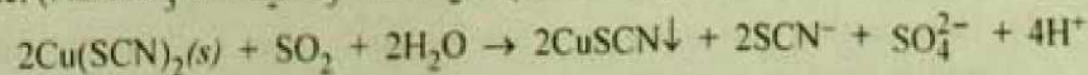


(6) Ammonium or potassium thiocyanate solution (0.1 M)

To 1-2 drops of the neutral or weakly acidic test solution add 1 drop of the thiocyanate solution. Black precipitate of $\text{Cu}(\text{II})$ thiocyanate appears, which slowly decomposes to white precipitate of $\text{Cu}(\text{I})$ - thiocyanate with liberation of thiocyanogen, $(\text{SCN})_2$ gas, as thiocyanate ion is oxidized by copper (II).



Black precipitate of $\text{Cu}(\text{SCN})_2$ on treatment with a reducing agent, such as, SO_2 -water, or, sodium bisulfite, (NaHSO_3 or $\text{Na}_2\text{SO}_3 + \text{dil. H}_2\text{SO}_4$), is readily transformed to white CuSCN .



(7) Metallic iron

Since, $E^\circ(\text{Fe}^{\text{II}}/\text{Fe}^\circ) = -0.44$ volt and $E^\circ(\text{Cu}^{\text{II}}/\text{Cu}^\circ) = +0.35$ volt, Cu^{2+} is reduced to metallic Cu° by Fe° , which is oxidized to Fe^{2+} . Insert a clean iron wire or a knife, or, a blade into a solution of $\text{Cu}(\text{II})$ salt and keep it as such for a few minutes. The iron is coated with a red deposit of metallic copper.



(8) Potassium ferrocyanide solution [$\text{K}_4\text{Fe}(\text{CN})_6$] (0.025M)

To 1-2 drops of neutral or weakly acidic (acetic acid) solution of the sample on a spot plate, add 1 drop of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution. Redish brown precipitate of $\text{Cu}(\text{II})$ -ferrocyanide appears if Cu^{2+} is present.



Iron, molybdenum and uranium interfere.

The precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ is insoluble in dilute acids (difference from uranium) but soluble in aqueous - NH_3 giving a blue solution. The precipitate is decomposed by NaOH , which transforms it into blue $\text{Cu}(\text{OH})_2$.

Fe^{II} gives white to pale blue precipitate of $\text{K}_2\text{Fe}[\text{Fe}(\text{CN})_6]$. Fe^{III} gives Prussian blue precipitate of $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$.

Molybdenum ferrocyanide is red-brown in colour, insoluble in dilute acid but readily soluble in solutions of caustic alkalies and ammonia (difference from uranyl and $\text{Cu}(\text{II})$ ferrocyanides). Uranyl ferrocyanide is soluble in dilute HCl (difference from copper). On treatment with NaOH solution, the brown precipitate of uranyl ferrocyanide turns yellow due to the formation of sodium diuranate, $\text{Na}_2\text{U}_2\text{O}_7$ (distinction from copper and molybdenum ferrocyanides).

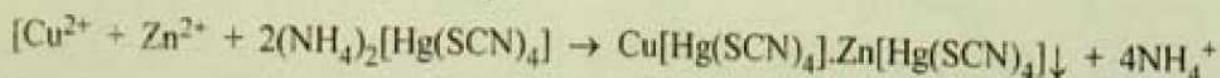
Confirmation

(i) Ammonium mercuri-thiocyanate & Zinc-acetate reagent

Reagent: (i) Dissolve 9g of ammonium thiocyanate and 8g of mercuric chloride in 100 ml of water.

(ii) 1% Zinc acetate in 2% NH_4Cl solution.

Place a minute drop of the neutral or weakly acidic (acetic acid) test solution on a spot plate, add 1 drop of 1% zinc acetate solution and 1 drop of ammonium mercuri-thiocyanate reagent. Stir with a glass rod. Deep violet crystalline precipitate appears due to coprecipitation of $\text{Cu}[\text{Hg}(\text{SCN})_4]$ and $\text{Zn}[\text{Hg}(\text{SCN})_4]$.



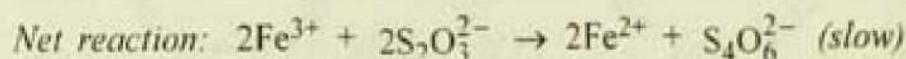
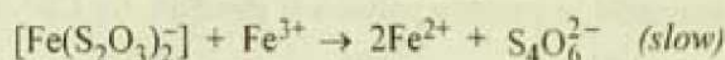
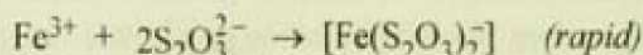
Note

- (1) Sequence of addition of the reagents and test solution should be maintained. Addition of Cu^{II} to $\text{Zn}[\text{Hg}(\text{SCN})_4]$ already formed has no effect.
- (2) This reaction also serves as a test for Zn^{2+} , when Cu^{II} acetate solution in dil. acetic acid is used as a reagent.

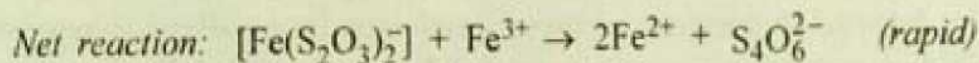
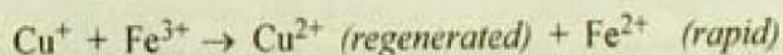
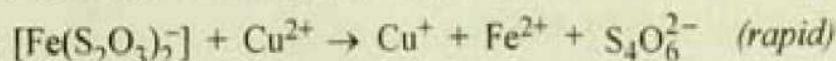
Co^{II} and Ni^{II} interfere, since they form blue and green precipitates of the corresponding mercurithiocyanato complexes, $\text{M}^{\text{II}}[\text{Hg}(\text{SCN})_4]$, $\text{M} = \text{Co}^{\text{II}}, \text{Ni}^{\text{II}}$. Fe^{III} ion interferes, forming blood red coloured $\text{Fe}^{\text{III}}(\text{SCN})^{2+}$ complex. Interference due to Fe^{III} ion may be eliminated by carrying out the test in presence of NH_4F or NH_4 -oxalate, which forms strong complexes with Fe^{III} and prevents its complex formation with SCN^- ion.

(2) Catalytic effect on Fe^{III} - thiosulfate reaction

Fe^{3+} ion rapidly reacts with thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ion to form violet coloured complex, $[\text{Fe}(\text{S}_2\text{O}_3)_2]^-$ ion, which slowly reacts with the remaining Fe^{3+} ions in solution with gradual disappearance of the violet colour. But in presence of Cu^{2+} ion, this latter reaction takes place rapidly.



Although Fe^{3+} ion is a hard Lewis acid but due to complex formation with softer $\text{S}_2\text{O}_3^{2-}$ ion, it is softened and the resulting complex $[\text{Fe}(\text{S}_2\text{O}_3)_2]^-$ is no longer hard, rather it is borderline or soft. As a result, if the borderline metal ion Cu^{2+} is present, the complex $[\text{Fe}(\text{S}_2\text{O}_3)_2]^-$ does not react with hard Fe^{3+} ion, but rather reacts with Cu^{2+} ions producing Cu^+ ion, which once formed, rapidly reacts with Fe^{3+} ion to regenerate Cu^{2+} ions, since $E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77$ volts is sufficiently greater than $E^\circ(\text{Cu}^{2+}/\text{Cu}^+) = 0.153$ volt.



This is how Cu^{2+} catalyses the reaction of Fe^{3+} with $\text{S}_2\text{O}_3^{2-}$ ion.

The reaction can also be carried out in presence of thiocyanate (SCN^-) ion, which forms blood red coloured $\text{Fe}(\text{SCN})^{2+}$ complex ion with Fe^{3+} . As this complex is very slightly dissociated in presence of sufficient excess of SCN^- ion, so the concentration of free Fe^{3+} ion is much less, hence the rate of its reaction with $\text{S}_2\text{O}_3^{2-}$ ions, in fact, rates of all the reactions in which Fe^{3+} ions participate, are appreciably lowered. As a result of this, the catalytic effect of Cu^{2+} ions becomes particularly evident under this condition.

The reaction velocity, i.e., the time required for decolourization, is employed for detection of minute amount of Cu^{2+} .

Place a drop of the test solution and a drop of distilled water on two adjacent cavities of a spot plate. Add 1 drop of Fe^{III} -thiocyanate reagent and 3 drops of 0.1N sodium thiosulfate solution to each of these cavities and mix uniformly with two separate glass rods.

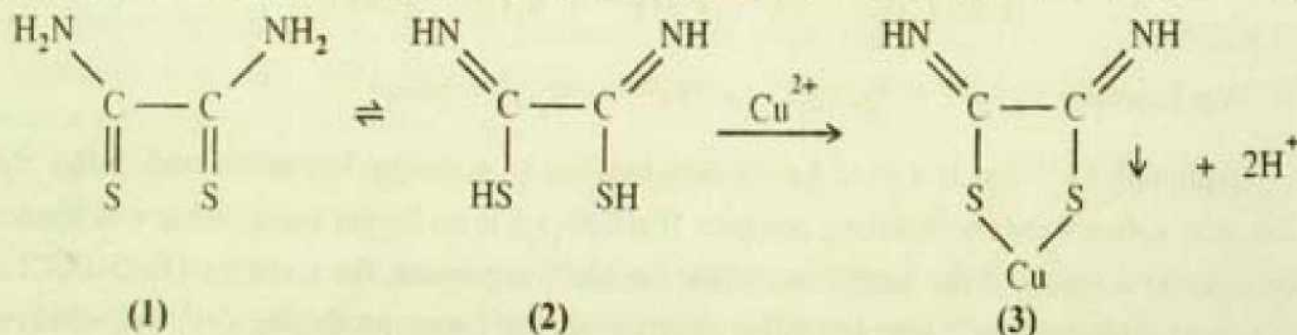
Decolourization of copper free (blank) solution requires ~1.5 to 2 minutes, whereas, decolourization of the test solution containing even a minute trace amount of Cu^{2+} ion is instantaneous.

Ferri-thiocyanate reagent: Dissolve ~1.5g of ferric chloride and 2g of KSCN or NH_4SCN in 100 ml of 0.01 M HCl.

(3) Rubeanic acid (dithioamide) test

Reagent: 0.5% solution of rubeanic acid in 95% ethanol. The reagent does not keep well in solution. Always freshly prepared reagent solution should be used.

Place a drop of the neutral test solution on a drop-reaction paper, expose the paper to NH_3 vapour by holding it over the open mouth of aqueous NH_3 solution. Add a drop of rubeanic acid (1 $\rightleftharpoons$ 2) reagent using a capillary dropper. A black to greenish-black spot due to copper rubeanate (3) is formed if Cu^{2+} is present. Insolubility of the precipitate in ammonia and organic solvents that dissolve rubeanic acid, suggests a polymeric structure for Cu^{II} -rubeanate complex.



Traces of Cu^{2+} , that may be present even in distilled water, also responds to this test. A blank test must always be carried out.

Limit of identification : 0.006γ of Cu

Limit of dilution : 1 : 2.5×10^6

Ni^{II} and Co^{II} if present, interfere by yielding blue and brown precipitates under the same condition. Copper may be detected in presence of these metal ions by capillary separation on the filter paper. The following procedure is recommended.

Impregnate a drop-reaction paper (Whatman No. 1) with the reagent solution and allow the paper to dry. Add a drop of the test solution acidified with acetic acid (~ 2M). If Ni^{II} and Cu^{II} are present, two circled zones will be formed. The central olive-green to black ring will be due to copper rubeanate and the outer blue-violet ring will be due to nickel rubeanate.

Limit of identification : 0.05γ of Cu in presen of 20,000 times of Ni.

Limit of dilution: 1 : 1×10^6

If Co^{II} and Cu^{II} are present, the central olive-green to black ring due to copper rubeanate will be surrounded by yellow-brown ring due to cobalt rubeanate.

Limit of identification : 0.25γ of Cu in pressem of 2000 times of Co

Limit of dilution : 1 : 2×10^6

Confirmatory test of copper through masking of interfering ions

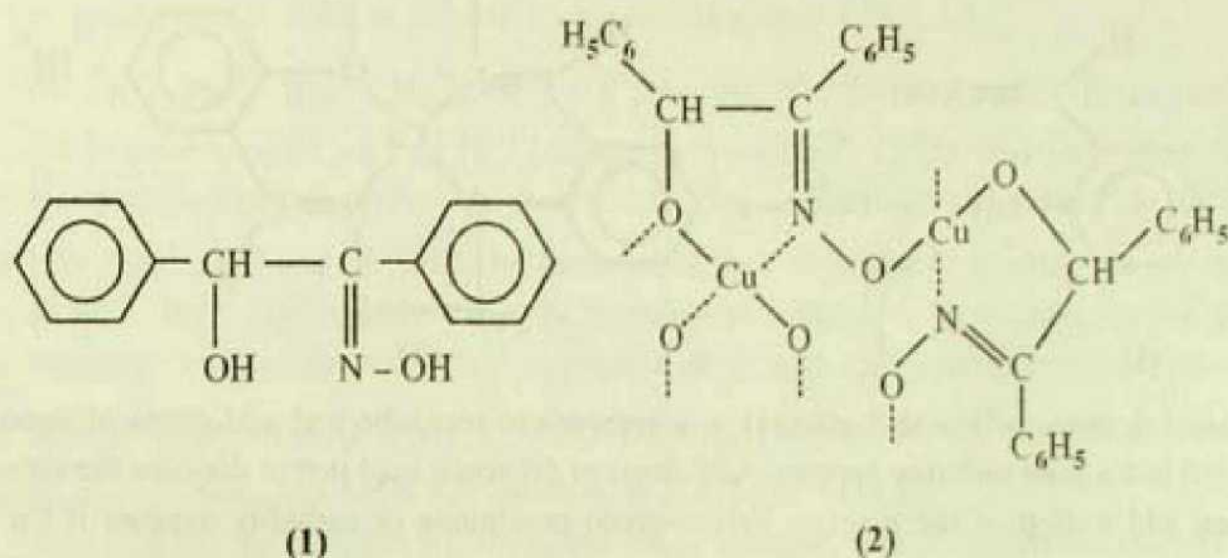
Place a drop of 20% aqueous malonic acid on a drop-reaction paper and add a drop of

the neutral test solution. Add 1 drop of 10% aqueous solution of ethylenediamine and then a drop 1% solution of rubenic acid in 95% ethanol. A green stain appears if Cu^{2+} is present.

(4) Test with α -benzoinoxime (or Cupron) reagent

Reagent: 5% solution of α -benzoin oxime in 95% ethanol.

α -Benzoin oxime (1) reacts with Cu^{2+} ion in weakly acidic solution to form green coloured innermetallic chelate complex (2), which because of its polymeric structure, does not even react with NH_3 to produce the deep blue complex $\text{Cu}(\text{NH}_3)_4^{2+}$ ion.



Metal ions which precipitate as hydroxides in presence of aqueous - NH_3 , should be kept in solution as tartarate complexes by adding NaK - tartarate. But large amount of tartarate and ammonium salts should be avoided, as Cu^{2+} ion is also complexed by tartarate and NH_3 and sensitivity of the reaction of Cu^{2+} may be lowered. If the test solution is strongly acidic, or, contains ammonium salts, evaporate the solution to dryness in a **FUME CUPBOARD**, then ignite with a drop of HNO_3 to decompose the NH_4^+ salts, cool and take up with a drop of dil.HCl before applying this test.

Place a drop of the weakly acidic test solution on a drop-reaction paper and allow the spot to dry. Add a drop of the α -benzoin oxime reagent and hold the paper over ammonia vapour. A green colouration will be observed if Cu^{2+} is present.

If the presence of other metal ions, particularly those forming hydroxide precipitates with aqueous - NH_3 are suspected, add a drop of 10% NaK-tartarate solution to the paper before the addition of α -benzoin oxime reagent.

Alternatively, impregnate a strip of a Whatman No. 1 filter paper with 5% ethanolic solution of α -benzoin oxime and allow the spot to dry. Cut the dry reagent paper into strips (1 mm $\times$ 10 mm). Dip one of these strips into a warm drop of the test solution and allow to stand for a few minutes and then hold the paper strip over a bottle of aqueous- NH_3 solution. A distinct green zone will develop in presence of Cu^{2+} ions.

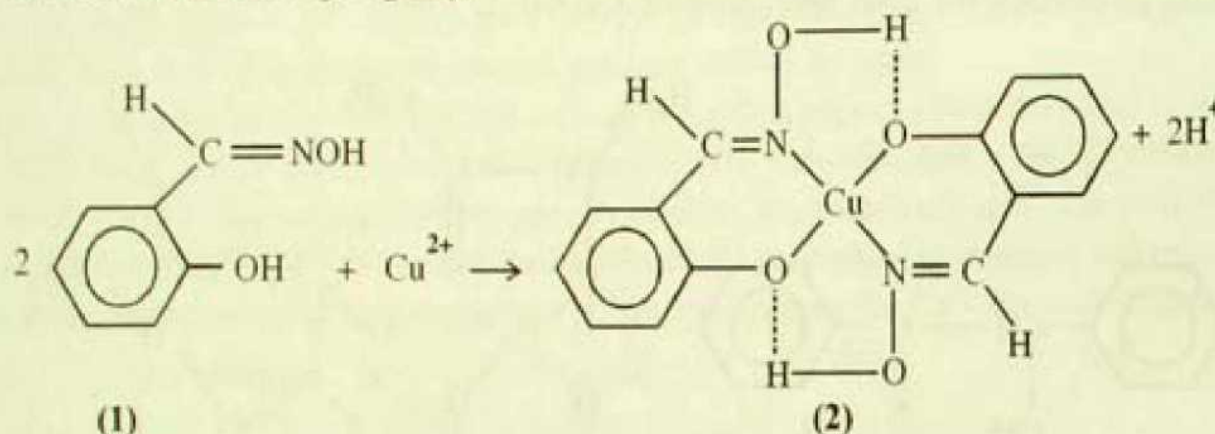
Limit of identification: 0.1 γ of Cu

Limit of dilution : 1 : 5×10^6

(5) Test with salicylaldoxime

Reagent: Dissolve 1g of salicylaldoxime in 5 ml of ethanol and add this solution to 95 ml of hot ($< 80^{\circ}\text{C}$) water. An oily suspension that is initially produced, almost disappears on gentle shaking. Filter and use the filtrate for the test.

Cu^{2+} reacts with salicylaldoxime (1) in weakly acidic solution to give a greenish yellow precipitate of the inner metallic complex, bis-salicylaldoximatocopper (II), (2), soluble in dilute mineral acids (HCl , HNO_3 , H_2SO_4).



Place 1-2 drops of the test solution in a semi-micro test tube and add drops of aqueous- NH_3 until just a faint turbidity appears. Add drops of dil. acetic acid just to dissolve the turbidity and then add a drop of the reagent. Yellow-green precipitate or turbidity appears if Cu^{2+} is present.

Limit of identification: 0.5γ of Cu

Limit of dilution : 1 : 1×10^6

4.7 Reactions of Cadmium (Cd^{II})

Indication

(1) Ignition test

When heated strongly with sodium oxalate in a dry test tube, cadmium compounds are reduced to metallic cadmium and form a metallic mirror surrounded by a brown stain of cadmium oxide,



When heated with a small amount of sulfur powder, the metallic mirror of Cd is transformed into yellow cadmium sulfide



Place a grain ($< 0.1\text{ g}$) of the solid sample mixed with an equal amount of sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$) in an ignition tube and heat strongly. A metallic mirror of Cd is produced with brown stains at the edges. Cool to room temperature and add a small amount ($< 0.1\text{ g}$) of sulfur powder avoiding contact with the wall of the ignition tube and heat again. The metallic mirror of Cd gradually transforms into orange CdS, which becomes yellow on cooling to room temperature.

Note: Cadmium oxide (CdO), formed on thermal decomposition of cadmium salts, varies in colour from greenish yellow through brown to nearly black depending up on temperature and duration of heating.

(2) H₂S-water or ZnS-slurry

Place a drop of the neutral or weakly acidic (<0.3M) test solution on a spot plate and add a drop of H₂S-water or ZnS slurry. Yellow precipitate of CdS is formed if Cd²⁺ is present.



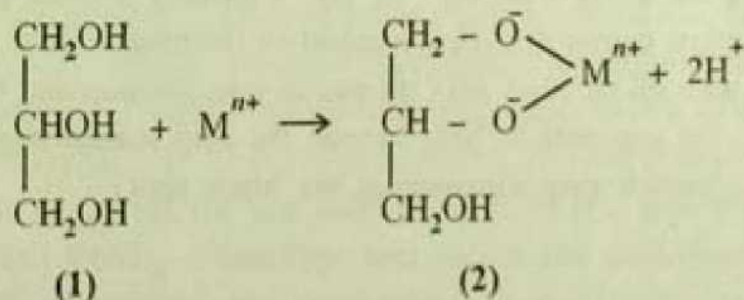
The precipitate of CdS is soluble in concentrated acid (<0.5 M).

N.B. Cu²⁺, Pb²⁺, Hg₂²⁺, Hg²⁺, Bi³⁺, Ag⁺, As (III, V), Sb (III, V) Sn (II, IV) interfere. But CdS is soluble in dil.~0.5 M HCl (difference from Hg²⁺, Cu²⁺), insoluble in ammonium sulfide and sodium sulfide (difference from As, Sb, Sn), insoluble in sodium sulfide (difference from Hg). Hg₂²⁺, Ag⁺ and Pb²⁺ may be removed as their chlorides by treating the test solution with dil.HCl. Pb²⁺, Hg²⁺ and Bi³⁺ may be removed as hydroxides by treating the test solution with aqueous - NH₃ solution. If Cu²⁺ is present along with Cd²⁺, both remain in solution as their ammine complexes, Cu(NH₃)₄²⁺ and Cd(NH₃)₄²⁺ after treatment with aqueous-NH₃. Copper may be removed from this mixture in a number of ways.

(i) By treating the solution with alkaline Na-K tartarate, which complexes both Cd²⁺ and Cu²⁺. If this mixture is boiled with glucose, Cu(II) tartarate complex is reduced and copper is precipitated as red coloured Cu₂O, which may be removed by centrifugation.

(ii) By adding drops of SO₂ - water or sodium bisulfite, in weakly acidic (~0.2 M) solution Cu²⁺ is reduced to Cu⁺, which is quantitatively precipitated as white CuSCN on addition of NH₄SCN or KSCN solution, keeping Cd²⁺ in solution. After separating CuSCN by centrifuging and then removing SO₂ by boiling, the centrifugate may be tested for Cd²⁺ with H₂S-water after reducing the acidity (<0.1 M).

(iii) If a solution containing Cd²⁺, Pb²⁺, Cu²⁺ and Bi³⁺ is treated with glycerol (1) in presence of excess of NaOH solution, Cd²⁺ is precipitated as its hydroxide, Cd(OH)₂, whereas, the other metal ions remain in solution as their glycerate complexes (2), which may be removed by centrifugation.



Take 1-2 drops of the test solution in a centrifuge tube and add equal volume of glycerol and a drop of NaOH solution (2M). Centrifuge and reject the centrifugate. Treat the precipitate

once again with glycerol and NaOH solution as before, centrifuge and discard the centrifugate to remove the last traces of Cu(II), Pb(II) and Bi(III) glycerates. Wash the precipitate with water by repeated centrifugation. To the white precipitate of $\text{Cd}(\text{OH})_2$ add 1 drop of H_2S -water. The precipitate turns yellow if Cd^{2+} is present.

(2a) Test of for Cd^{2+} by capillary separation

Place a drop of the weakly acidic ($< 0.3 \text{ M}$) test solution on a drop reaction paper and allow the spot to dry. Add 1 drop of H_2S - water using a capillary dropper. Blackening occurs if Hg_2^{2+} , Hg^{2+} , Bi^{3+} and Cu^{2+} are present along with Cd^{2+} . Now slowly add dil.HCl ($\sim 1 \text{ M}$) on the black spot using a capillary dropper. A wet zone surrounding the black spot, gradually moves out of the black spot towards the periphery of the paper. Dry the paper and hold it over a bottle of ammonia. A yellow ring or a yellow zone is formed outside the black spot if Cd^{2+} is present.

Due to comparatively higher solubility of CdS over the sulfides of mercury, copper, lead and bismuth, although CdS is precipitated in weakly acidic ($< 0.3 \text{ M}$) medium, but it dissolves if the acidity is higher ($\sim 1 \text{ M}$). pK_{sp} values (at 25°C) of the sulfides precipitating in dil.HCl medium are given below:

	CdS	PbS	CuS	Cu_2S	HgS	Ag_2S	Bi_2S_3	ZnS
pK_{sp} :	26.1	26.6	35.2	47.6	~ 52	49.2	97	24

Due to marked difference in the pK_{sp} values of the sulfides, capillary separation of Cd^{2+} from Cu^{2+} , Cu^+ , Hg^{2+} , Ag^+ and Bi^{3+} may be possible by this technique, but such separation of Cd^{2+} from Pb^{2+} may not be possible, as the pK_{sp} values of CdS and PbS are very close.

Instead of using H_2S - water as the reagent for this test, a slurry of freshly precipitated zinc sulfide (ZnS) may also be used. Since the solubility product of HgS, Ag_2S , Bi_2S_3 etc., are much lower than that of ZnS, the corresponding metal ions react with white coloured ZnS and snatches the S^{2-} ion to produce the characteristically coloured precipitates of their own sulfides on the surface of white ZnS.



Now, if Cd^{2+} is present along with Cu^{2+} or Hg^{2+} , initially a black precipitate or a black spot is formed as the yellow colour of CdS is masked by the black colour of copper or mercury sulfides. On treatment with dil.HCl ($\sim 1 \text{ M}$) CdS passes into solution and Cd^{2+} ions move away due to capillary action. On exposure to NH_3 vapour, the acid is neutralized, and CdS is again precipitated, forming a yellow ring surrounding the black spot.

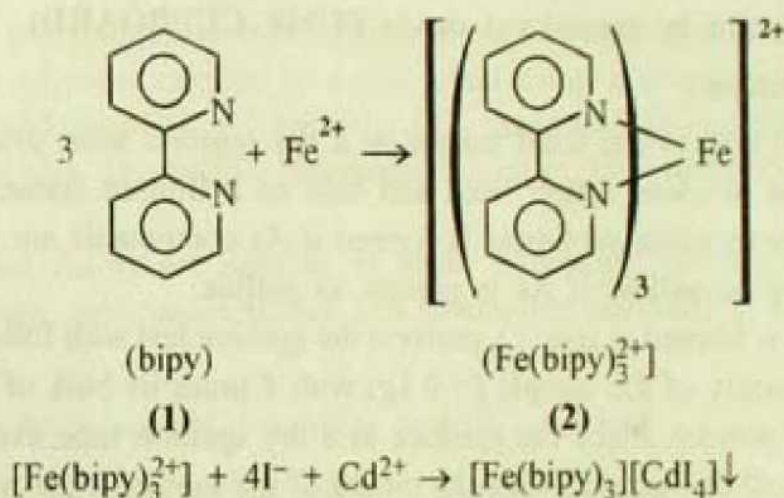
Confirmation

(1) Test with tris-bipyridyl Fe^{II} iodide, $[\text{Fe}(\text{bipy})_3]^{2+}(\text{I}^-)_2$ reagent

Reagent: Dissolve 0.15 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or 0.2 g of Mohr's salt $[(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}]$ and 0.25 g of 2, 2'-bipyridine in 50 ml of 0.01 M HCl or HNO_3 (prepared from AR samples).

Add 10 g of KI and shake vigorously for ~30 minutes. Filter off the deep red coloured precipitate of $[\text{Fe}(\text{bipy})_3]\text{I}_2$. The filtrate is a saturated solution of this salt and contains sufficient excess of iodide ion to accomplish the formation of the complex ion, $[\text{CdI}_4]^{2-}$, which is essential for this test. The reagent solution is quite stable. If any turbidity appears, the solution should be filtered before use.

In weakly acidic medium ($\sim 0.01\text{ M}$) Fe^{2+} ion reacts with 2, 2'-bipyridine (bipy, 1) to form the red coloured *tris*-bipyridyliron (II) complex, $[\text{Fe}(\text{bipy})_3]^{2+}$ ion (2). This complex cation combines with large size anions, such as $[\text{CdI}_4]^{2-}$, $[\text{HgI}_4]^{2-}$, $[\text{Ni}(\text{CN})_4]^{2-}$ etc. to form red coloured crystalline compounds. At high concentration of iodide ion, the iodide salt, $[\text{Fe}(\text{bipy})_3]\text{I}_2$ precipitates. The precipitation of red-violet coloured $[\text{Fe}(\text{bipy})_3][\text{CdI}_4]$ maybe used for detection of Cd^{2+} if a saturated solution of $[\text{Fe}(\text{bipy})_2]\text{I}_2$ in presence of excess of I^- ion is used as the reagent.



Place 1 drop of the neutral or weakly acidic or ammoniacal test solution on a drop-reaction paper and add 1 drop of the reagent using a capillary dropper before the test solution is absorbed by the paper. The reaction occurs at once. An intense red fleck or a ring is formed at the centre due to precipitation of the cadmium complex, which becomes visible against the reagent colour, that spreads throughout the paper.

Limit of identification : 0.05γ of Cd

Limit of dilution : 1 : 1×10^6

Metal ions such as Ag^+ , Tl^+ , Pb^{2+} , Hg^{2+} etc. which form insoluble precipitates with I^- interfere. Cu^{2+} in neutral or weakly acidic solution oxidizes iodide to iodine and itself is reduced and precipitated as Cu_2I_2 , which appears brown due to adsorption of iodine. Mercury, tin, antimony, bismuth salts form soluble complexes with large excess of I^- and such complexes also combine with $[\text{Fe}(\text{bipy})_3]^{2+}$ to yield red precipitates. If these interfering ions are suspected, prior to applying this test, treat the test solution with dil.HCl and dil. H_2SO_4 , to precipitate AgCl , TlCl , PbCl_2 and PbSO_4 . Centrifuge and render the centrifugate ammoniacal, when mercury and bismuth, if present, are precipitated as hydroxides or oxides. Remove any precipitate formed at this stage by centrifugation. The clear ammoniacal centrifugate contains $\text{Cu}(\text{NH}_3)_4^{2+}$ and $\text{Cd}(\text{NH}_3)_4^{2+}$ ions. If this ammoniacal test solution is treated with the reagent,

$\text{Cu}(\text{NH}_3)_4^{2+}$, due to its higher stability remains unreactive, whereas, $\text{Cd}(\text{NH}_3)_4^{2+}$, due to its lower stability, reacts promptly with the reagent. Zn^{2+} if present, remains as $\text{Zn}(\text{NH}_3)_4^{2+}$ in the ammoniacal extract and does not react with the reagent.

Limit of identification:

0.08γ of Cd in presence of 5000 times this amount of Cu.

0.01γ of Cd in presence of 5000 times this amount of Zn.

4.8. Reactions of Arsenic (As^{III} , AsO_3^{3-} , As^{V} , AsO_4^{3-})

Caution: All As compounds are poisonous. Only small quantity (<0.1 g) should be used for tests avoiding physical contact with the materials.

Indication

(1) **Ignition test:** (To be carried out inside **FUME CUPBOARD**)

Sublimate formation

Place a grain (<0.1 g) of the solid sample in a dry ignition tube, plug the mouth of the test-tube with a piece of clean cotton wool and heat on a Bunsen flame, slightly tilting the test tube. A steel-grey to white sublimate is formed if As compounds are present. The colour of the sublimate may be yellow if As is present as sulfide.

(2) If a sublimate is formed in test (1), perform the ignition test with following modification.

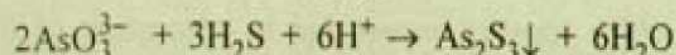
Mix a minute quantity of the sample (< 0.1g) with 4 times its bulk of anhydrous Na_2CO_3 and a little charcoal powder. Place the mixture in a dry ignition tube avoiding adherence of the particles to the wall of the tube. Plug the mouth of the ignition tube with a piece of clean cotton wool and heat the contents on a Bunsen flame, holding the tube slightly tilted. A brownish-black mirror due to elemental As is formed if As is present.



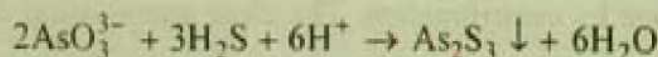
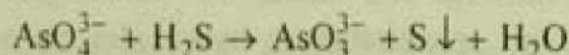
(3) H_2S - water

To 1 drop of neutral or weakly acidic test solution add 1 drop of H_2S -water.

As(III): Yellow precipitate of As_2S_3 is formed if As is present as $\text{As}(\text{III})/\text{AsO}_3^{3-}$.



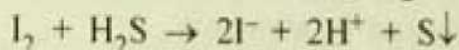
As(V) : No immediate precipitate is formed, but on adding an excess of H_2S -water, yellow precipitate of As_2S_3 slowly appears with separation of milky white colloidal sulfur, due to oxidation of H_2S by $\text{As}(\text{V})$:



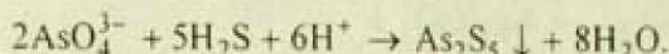
If a milky solution results on addition of H_2S -water, reduce As(V) to As(III) by adding 1-2 drops of SO_2 -water before adding H_2S -water, boil off the excess of SO_2 , and then add H_2S -water. Alternatively, add 1 drop of KI solution ($\sim 0.1M$) which acts as a catalyst in the reduction of As(V) to As(III) .



The I_2 that is liberated is reduced by H_2S to regenerate I^- , which is the catalyst.



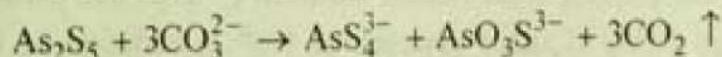
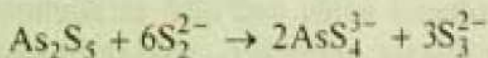
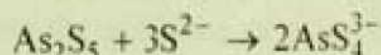
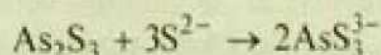
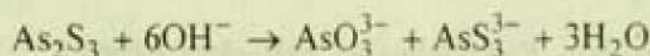
In presence of large excess of conc. HCl , however, yellow precipitate of arsenic pentasulfide (As_2S_5) is formed,



(4) Test with precipitated arsenic sulfides

Centrifuge the precipitated arsenic sulfide, reject the centrifugate and place the slurry of the residue on the adjacent cavities of a spot plate using a dropper. Add 1 drop of NaOH ($\sim 2M$)/ Na_2CO_3 ($\sim 0.5M$)/ aq-NH_3 (1:1)/ $(\text{NH}_4)_2\text{CO}_3$ (saturated)/ $(\text{NH}_4)_2\text{S}/(\text{NH}_4)_2\text{S}_x$ respectively on the different cavities. The yellow precipitate dissolves, but reappears on acidification with dil. HCl .

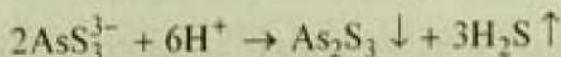
Both As_2S_3 and As_2S_5 are soluble in alkali hydroxide, ammonia, sodium carbonate, ammonium carbonate, ammonium sulfide and ammonium polysulfide, forming oxy-, oxythio- and thio-salts:



[AsO_3^{3-} : arsenite, AsS_3^{3-} : thioarsenite; AsO_4^{3-} : arsenate, $\text{AsO}_3\text{S}^{3-}$: oxythioarsenate,

AsS_4^{3-} : thioarsenate]

Thio salts of As(III) and As(V) decompose on acidification, with precipitation of the corresponding sulfides and evolution of H_2S . Excess polysulfide, if present, is also decomposed by acid, producing colloidal milky sulfur with liberation of H_2S .



Oxythio-salts may be transformed to thio-salts by reacting with H_2S ,



Resulting thiosalts are decomposed by acid accordingly.

(4) Silver nitrate solution (0.1 M)

As (III): Yellow precipitate of silver arsenite (Ag_3AsO_3) is formed in neutral solution. The precipitate is soluble in dilute mineral acids and in ammonia.

As (V): Brownish-red precipitate of silver arsenate (Ag_3AsO_4) is formed in neutral solution. The precipitate is soluble in dilute mineral acids and in ammonia, but insoluble in acetic acid:



Note: CrO_4^{2-} , $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$ with which Ag^+ forms coloured precipitates, that are insoluble in acetic acid, interfere in this test.

Place a drop of the test solution in a semi-micro test tube and add a few drops concentrated NH_3 and a few drops of "10-volume" H_2O_2 . Warm the mixture and acidify with acetic acid. Add 1-2 drops of AgNO_3 solution. A brownish red precipitate appears if As is present.

Note: In ammoniacal medium H_2O_2 oxidizes As(III) to As (V):

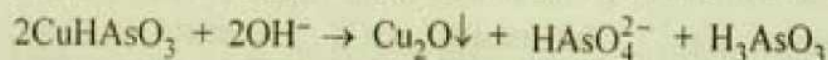


5. Test with CuSO_4 solution : Formation of Scheele's green

In neutral solution arsenite (AsO_3^{3-}) reacts with Cu^{2+} ion to produce a green precipitate of copper (II) arsenite, formulated as CuHAsO_3 and $\text{Cu}_3(\text{AsO}_3)_2 \cdot x\text{H}_2\text{O}$, popularly known as *Scheele's green*.



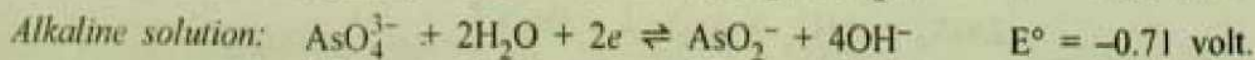
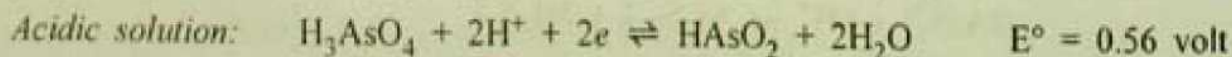
The precipitate is soluble in dilute mineral acids and also in aqueous ammonia solution producing blue solution. On boiling with NaOH solution ($\sim 2M$) the precipitate dissolves and red precipitate of cuprous oxide (Cu_2O) appears as Cu^{II} is reduced to Cu^{I} by As^{III} ,



Confirmation

(1) Reversible redox reaction with $\text{I}_2/2\text{I}^-$ couple

Formal potential (E^f) of $\text{I}_2/2\text{I}^-$ couple ($E^\circ = +0.53\text{V}$) is independent of pH upto pH~8, whereas, the E^f values of $\text{AsO}_4^{3-} / \text{AsO}_3^{3-}$ couple are pH dependent:



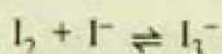
Thus, arsenite (AsO_2^- or AsO_3^{3-}) is oxidized to arsenate (AsO_4^{3-}) by iodine-iodide mixture (I_2/I^- , ie, triiodide, I_3^-) in basic solution, on the other hand, in strongly acidic medium, arsenic acid (H_3AsO_4) oxidizes iodide to iodine, which combines with excess I^- to form the triiodide I_3^- ion. The whole reaction sequence can be made reversible by adjustment of acidity (*cf. Sect 2.4*). If the reaction is carried out in presence of starch indicator, the reversible colour change from blue (I_2) to colourless (I^-) to blue (I_2) may be observed.

Arsenite (AsO_3^{3-}) decolourizes the brown colour of I_3^- (or blue colour of starch - I_3^-) according to,



The reaction can be made to proceed to the right by removing the liberated H^+ ions with a buffer solution of $\text{pH} \approx 8$. This can be accomplished by adding sodium bicarbonate solution.

Arsenate (AsO_4^{3-}) oxidizes I^- to liberate I_2 in presence of strong acid. Liberated I_2 combines with I^- ion to form I_3^- ion.



This can be achieved by adding conc.HCl to the reaction mixture.

Test for AsO_3^{3-}

Place one drop of starch indicator and 1 drop of I_2/KI mixture on a spot plate. A blue colouration will be produced. Add 1 drop of sodium bicarbonate solution and mix with a glass rod. The blue colour remains as such. Now add 1 drop of the neutral or weakly acidic test solution and if necessary 1-2 more drops of the NaHCO_3 solution. Discharge of the blue colour will indicate the presence of arsenite or other reducing agents. Now add 1-2 drops of conc.HCl. Reappearance of the blue colour will indicate the presence of reversible $\text{AsO}_4^{3-} / \text{AsO}_3^{3-}$ and $\text{I}_2/2\text{I}^-$ systems.

Test for AsO_4^{3-}

Place 1 drop of the test solution and one drop of KI solution (0.1 M) and 1 drop of starch indicator on a spot plate or on a drop reaction paper. Add 1 drop of conc.HCl. Appearance of blue colour indicates the presence of arsenate or other oxidizing agents that can oxidize I^- to I_2 . Now add drops of NaHCO_3 solution. Discharge of blue colour will indicate the presence of reversible redox systems like $\text{AsO}_4^{3-} / \text{AsO}_3^{3-}$ and $\text{I}_2/2\text{I}^-$.

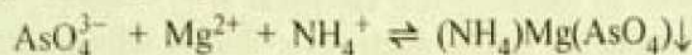
(2) Magnesia mixture-ammonia solution

Reagent: Dissolve 10.2g of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and 10.7 g of NH_4Cl in water and dilute to 50 ml with water and add 5 ml of conc. NH_3 .

To 1 ml of the test solution in a semi-micro test tube, add 1 ml of the reagent and a few drops of aq- NH_3 to render the solution ammoniacal.

As(III): Arsenite forms no precipitate with magnesia mixture.

As(V): Arsenate forms white crystalline precipitate of ammonium magnesium arsenate hexahydrate, $(\text{NH}_4)\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$, soluble in dilute mineral acids.



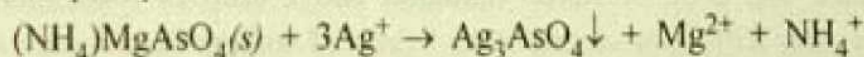
Note: Phosphate gives similar crystalline precipitate, $(\text{NH}_4)\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ with magnesia mixture and therefore interferes. If phosphate is present, the test should be performed with magnesia mixture prepared from $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, NH_4NO_3 and NH_3 instead of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, NH_4Cl and NH_3 .

(2a) $\text{Mg}(\text{NO}_3)_2 - \text{NH}_4\text{NO}_3 - \text{NH}_3$ reagent

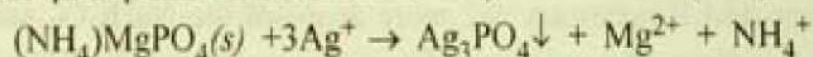
Dissolve ~13g of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 16g of NH_4NO_3 in water, add 5 ml of conc. NH_3 and dilute to 1000 ml with water.

Take 1-2 drops of the neutral or weakly acidic test solution in a semi-micro test tube, add drops of conc. NH_3 to render it ammoniacal. Add 1-2 drops of "10-volume" H_2O_2 and warm (to oxidize arsenite to arsenate). To the warm solution add 1-2 drops of $\text{Mg}(\text{NO}_3)_2 - \text{NH}_4\text{NO}_3 - \text{NH}_3$ reagent and shake well. White crystalline precipitate appears if AsO_4^{3-} or PO_4^{3-} or both are present. If AsO_3^{3-} is present, it is oxidised to AsO_4^{3-} by the H_2O_2 treatment. Centrifuge and reject the centrifugate. Treat the white precipitate with a few drops of dil. acetic acid and 1-2 drops of silver nitrate solution.

If AsO_4^{3-} is present: The precipitate is transformed to red silver arsenate.



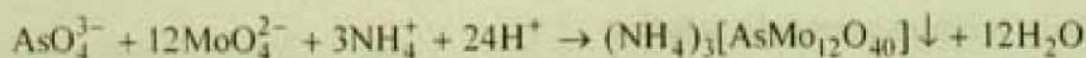
If PO_4^{3-} is present: The precipitate is transformed to yellow silver phosphate.



(3) Ammonium molybdate test

Reagent: Dissolve ~4.5g of ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ in a mixture of 5-6 ml of conc. NH_3 and 4-5 ml of water. Add 12g of NH_4NO_3 and complete the dissolution. Dilute the solution to 100 ml. Allow to stand over night, filter if necessary. Before adding this reagent to the test solution, it should be ensured that the test solution has been made sufficiently acidic by adding conc. HNO_3 .

To 1-2 drops of the test solution in a semi-micro test tube add a 1 ml of conc. HNO_3 and 1 ml of ammonium molybdate reagent and boil. Crystalline yellow precipitate of ammonium arsenomolybdate, $(\text{NH}_4)_3[\text{AsMo}_{12}\text{O}_{40}]$ appears.

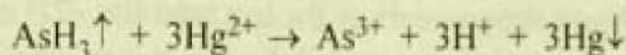
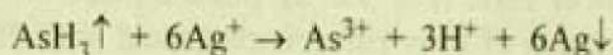
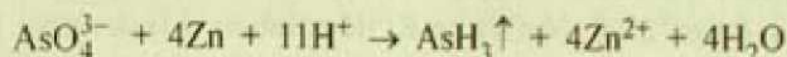
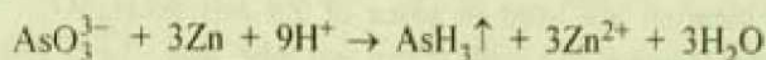


Arsenite normally does not give any precipitate with ammonium molybdate. But when the sample is boiled with conc. HNO_3 and the reagent, AsO_3^{3-} is oxidized to AsO_4^{3-} by hot conc. HNO_3 and eventually responds to this test. Phosphate gives similar yellow precipitate of

ammonium phosphomolybdate in the cold or on gentle warming, whereas, boiling is required for precipitation of ammonium arsenomolybdate (difference from phosphate). Precipitates of both ammonium arsenomolybdate and phosphomolybdate are insoluble in HNO_3 but are soluble in ammonia and NaOH solution due to dissociation of the heteropoly anions, phosphomolybdate and arsenomolybdate, $[\text{EMo}_{12}\text{O}_{40}]^{3-}$, ($\text{E} = \text{P}, \text{As}$). Ammonium arsenomolybdate passes into solution when boiled with tartaric acid (distinction from phosphate). Tartarate forms complex with molybdate of such stability that only phosphomolybdate can be formed but not arsenomolybdate.

(4) Gutzeit test

Arsenic compounds on treatment with zinc dust and $\text{dil. H}_2\text{SO}_4$ produce arsine (AsH_3) gas, which reduces silver nitrate to metallic silver and mercuric chloride to/or mercuric bromide to metallic mercury.



Take $\sim 1\text{g}$ of arsenic free zinc dust in a test tube and add $\sim 5\text{ ml}$ of dilute H_2SO_4 . Loosely plug the test tube with a piece of pure cotton wool and then place a piece of Whatman No. 1 filter paper impregnated with a drop of 20% silver nitrate solution on the top of the test tube (Fig. 3.27 a). Warm the test tube gently in a **FUME CUPBOARD** for about ~ 2 minutes. Remove the filter paper and examine the part of the paper that covered the mouth of the test tube. A light brown spot may be observed due to the presence of traces of arsenic in the reagents.

Now remove the cotton wool plug and add $\sim 1\text{ ml}$ of the sample solution (or, $\sim 0.1\text{g}$ of the solid sample) to the test tube and replace the cotton wool plug as before. Shift the silver nitrate paper on the top of the tube in such a manner that a fresh portion of it is exposed to issuing gas. Warm if necessary to ensure that the rate of evolution of gas remains nearly the same as before. Remove the filter paper after ~ 2 minutes and compare the two spots due to metallic silver. The second spot will appear black if much arsenic is present.

Note

(1) The test may be performed directly on the solid sample, on solutions of the sample and more appropriately using the yellow precipitate obtained in the ammonium molybdate test, or, the white precipitate obtained in the magnesia mixture test. The corresponding precipitates obtained with phosphate do not respond to Gutzeit test.

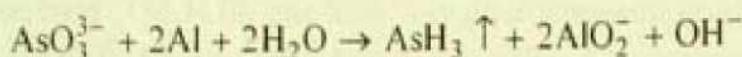
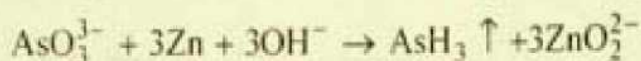
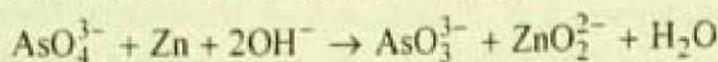
(2) H_2S , PH_3 and SbH_3 also render silver nitrate paper black. These may be rendered harmless by using purified cotton wool plug impregnated with 10% cuprous chloride solution.

Limit of identification: 1γ of As

Limit of dilution: $1 : 5 \times 10^4$

(5) Fleitmann's test

As (III) compounds react with Al or Zn metal in presence of caustic alkali to liberate arsine (AsH_3) gas. As (V) compounds under this condition, are reduced to As(III) compounds, but antimony compounds are not affected by this reagent. This test thus offers a means of differentiating between arsenic and antimony compounds.



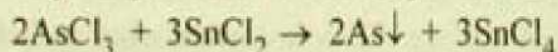
The test may be conducted in the same way as the Gutzeit test described before, except Zn or Al and NaOH solution are used in place of Zn and dil. H_2SO_4 .

Place 1 ml of the test solution in a semi-micro test tube, add ~1g of Zn(or Al) metal powder (free from As) and 1 ml of 2 M NaOH or KOH solution. Fix a small glass dropper at the mouth of the test tube with a rubber cork. (Fig. 3.27b), place a piece of purified cotton wool inside the dropper tube. Place a piece of filter paper impregnated with 20% AgNO_3 solution on the top of the dropper tube. Warm the contents of the test tube for ~2-3 minutes and examine the filter paper. A yellow to gray stain is produced if As is present. The apparatus as shown in the Fig. 3.27b should be used to avoid contact of the AgNO_3 paper with alkali.

(6) Bettendorff's test

Reagent: Saturated SnCl_2 solution in conc.HCl.

When warmed with saturated stannous chloride solution in presence of conc.HCl, arsenic compounds are reduced to dark brown, finally black elemental arsenic,



Only mercury compounds interfere, as these are also reduced to grey to black metallic mercury. Interference due to mercury may be eliminated by converting arsenic into arsenate and precipitating ammonium-magnesium arsenate, followed by heating to redness. By this treatment arsenic is transformed to magnesium pyroarsenate ($\text{Mg}_2\text{As}_2\text{O}_7$) and mercury salts, if any, are volatilized. This is the basis of this delicate test for arsenic.

Take 1-2 drops of the test solution or a grain (<0.1g) of the sample in a small porcelain or silica crucible, add 1-2 drops of conc. NH_3 and 2 drops of "10-volume" H_2O_2 to oxidize any As(III) to As(V). Add 2 drops of magnesium sulfate solution (~0.5 M). Evaporate the mixture slowly by gentle warming to dryness in a **FUME CUPBOARD** and finally heat strongly until fuming ceases. Cool somewhat and add 1-2 drops of a saturated solution of SnCl_2 in conc.HCl and warm gently. A brown to black precipitate or colouration is produced if As is present.

Limit of identification : 1γ of As

Limit of dilution: 1 : 5×10^4

4.9 Reactions of Antimony (Sb^{III} , Sb^{V})

Indication

No characteristic dry test may be recommended for Sb.

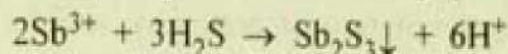
Antimony compounds maybe obtained in solution by extracting the solid samples with conc.HCl/NaOH solution/ Na_2CO_3 solution.

(1) Tests with H_2S -water

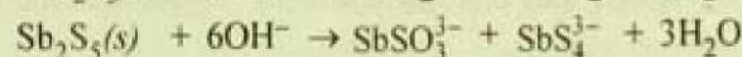
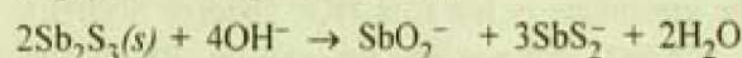
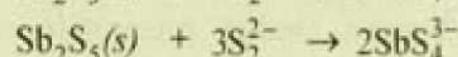
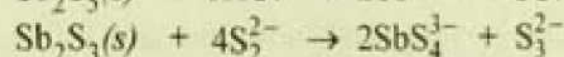
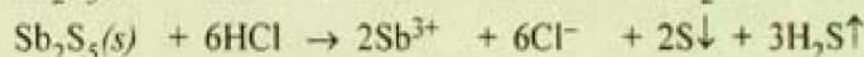
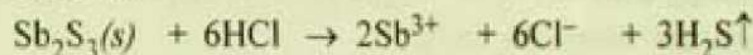
To 1-2 drops of neutral or weakly acidic test solution add equal volume of H_2S - water.

Sb(III): Orange red precipitate of antimony trisulfide (Sb_2S_3) appears.

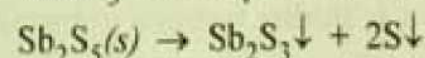
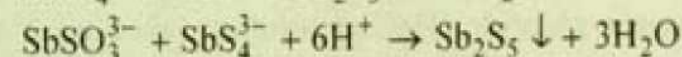
Sb(V): Orange red precipitate of antimony pentasulfide (Sb_2S_5) appears.



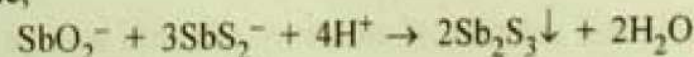
Both the precipitated sulfides (Sb_2S_3 and Sb_2S_5) are soluble in warm concentrated HCl (distinction from arsenic and mercury sulfides), ammonium sulfide, ammonium polysulfide, alkali hydroxides forming respectively antimony trichloride, thio-, oxy-, and oxythioantimonates (III) and antimonates (V).



Solutions of thio- and oxythio-salts of antimony (III and V) on acidification with HCl initially precipitate Sb_2S_5 , which ultimately decomposes to trisulfide with separation of sulfur.

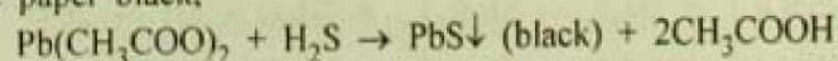


Antimonite (SbO_2^-) and thioantimonite (SbS_2^-) mixture on acidification precipitates antimony trisulfide,



Centrifuge the orange-red precipitate obtained on treatment of the test solution with H_2S -water, reject the centrifugate. Divide the orange-red precipitate into 3 parts and perform the following tests:

1(a) Part-1. Take one part of the precipitate in a semi-micro test tube, add a few drops of conc.HCl and warm. The precipitate passes into solution with evolution of H_2S gas which turns lead acetate paper black,



Place the remaining 2 parts of the precipitate into two adjacent cavities of a spot plate and treat as follows:

1(b) Part-2: Add 1-2 drops of ammonium sulfide to the orange red precipitate. The precipitate dissolves. Acidify the mixture by adding drops of dil.HCl solution. The orange-red precipitate reappears.

1(c) Part-3: Add 1-2 drops of dil.NaOH solution (~2M) to the orange red precipitate. The precipitate passes into solution. Acidify the mixture by adding drops of dil.HCl. The orange red precipitate reappears.

If tin is present in Sn(IV) state as SnCl_4 along with Sb(III) or Sb(V), only antimony sulfides may be precipitated by H_2S in dil.HCl medium keeping Sn(IV) in solution by adding some oxalic acid, $(\text{COOH})_2$, which keeps Sn(IV) in solution by forming a complex ion of the type, $[\text{Sn}(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{4-}$, but does not affect precipitation of antimony sulfides.

Separation of Sb and Sn

To 1 ml of the weakly acidic test solution in a semi-micro test tube, add drops of H_2S -water to precipitate completely antimony and tin sulfides. Centrifuge and discard the centrifugate. Warm the orange-yellow precipitate with ~1 ml of conc.HCl. The precipitate passes into solution in which antimony exists as $\text{H}[\text{Sb}^{\text{III}}\text{Cl}_4]$ and tin as $\text{H}_2[\text{Sn}^{\text{IV}}\text{Cl}_6]$. Divide the solution into two parts and perform the following tests.

1(d) Part-1:

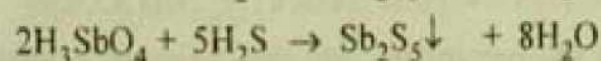
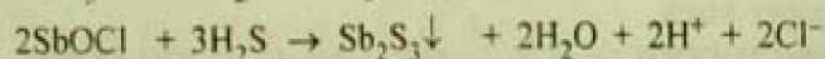
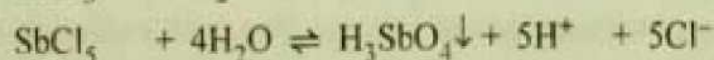
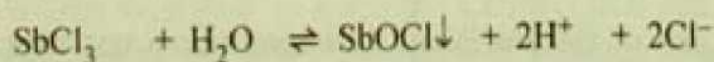
Render the solution ammoniacal with (1:1) aq- NH_3 solution, add a few crystals of oxalic acid, heat to boiling and add drops of H_2S -water. Orange precipitate of Sb_2S_3 appears. Centrifuge and dissolve the precipitate in hot conc.HCl. Oxidize Sb(III) to Sb(V) by adding a few crystals of NaNO_2 or KNO_2 and confirm antimony by Rhodamine-B test (p-275).

1(e) Part-2:

Neutralize the acidic test solution partly by adding a few grains of Na_2CO_3 , add a few pieces of iron nails and warm gently. Iron (Fe) reduces Sb(III) to precipitate elemental Sb on the iron nails. Sn (IV) is reduced to Sn(II). Centrifuge and add a few drops of the clear centrifugate to 1 drop of mercuric chloride (HgCl_2) solution taken on a spot plate. White precipitate of Hg_2Cl_2 changing to grey as Hg_2Cl_2 , is further reduced to metallic Hg, indicating the presence of Sn(II).

(2) Dilution with water

Pour 1-2 drops of the acidic test solution of antimony salt into a large volume (~25 ml) of water contained in a small beaker. White precipitates of basic salts of Sb(III) and oxyacid of Sb(V) appear, which on treatment with 1-2 drops of H_2S -water, transform to orange-red antimony sulfides.

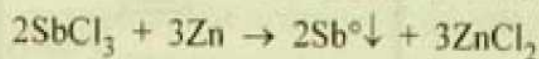


(3) Reduction to element by metallic Zn, Sn and Fe

E° values in acid medium of the $\text{Sb}^{\text{V}}/\text{Sb}^{\text{III}}$, $\text{Sb}^{\text{III}}/\text{Sb}^\circ$, $\text{Sn}^{\text{IV}}/\text{Sn}^{\text{II}}$, $\text{Sn}^{\text{II}}/\text{Sn}^\circ$, $\text{Fe}^{\text{II}}/\text{Fe}^\circ$ and $\text{Zn}^{\text{II}}/\text{Zn}^\circ$ couples are given below:

Couples	$\text{Sb}^{\text{V}}/\text{Sb}^{\text{III}}$	$\text{Sb}^{\text{III}}/\text{Sb}^\circ$	$\text{Sn}^{\text{IV}}/\text{Sn}^{\text{II}}$	$\text{Sn}^{\text{II}}/\text{Sn}^\circ$	$\text{Fe}^{\text{II}}/\text{Fe}^\circ$	$\text{Zn}^{\text{II}}/\text{Zn}^\circ$
$E^\circ(\text{volt})$	+0.64	+0.212	+0.15	-0.136	-0.44	-0.76

The E° values reveal that (i) Sb^{V} may be reduced to Sb^{III} by SnCl_2 solution and (ii) Sb^{V} and Sb^{III} are reduced to elemental (Sb°) state by metallic Sn, Fe and Zn.



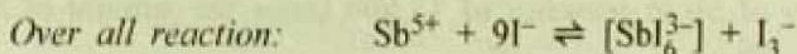
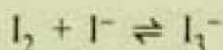
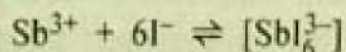
Trace amount of stibine (SbH_3) is also produced when reduced with Zn. It is preferable to use metallic tin or metallic iron for reduction of $\text{Sb}(\text{III})$ and $\text{Sb}(\text{V})$ to Sb° .

Take a drop of the acidic test solution on a platinum foil and place a small clean Zn granule on the platinum foil so that the Zn foil is in contact with the test solution. A black stain is formed on the platinum foil - if antimony is present.

Now remove the Zn granule and dissolve the black stain in a small volume of hot dilute HNO_3 . Transfer 1 drop of this HNO_3 extract on to a spot plate and add 1 drop of H_2S -water. Orange red precipitate of antimony sulfide is formed.

(4) Potassium iodide (0.1 M) solution

In acid medium Sb^{V} oxidizes I^- to liberate I_2 . [$E^\circ(\text{Sb}^{\text{V}}/\text{Sb}^{\text{III}}) = +0.64$ volt, $E^\circ(\text{I}_2/2\text{I}^-) = +0.53$ volt] and itself is reduced to hexaiodoantimonate (III), $[\text{SbI}_6^{3-}]$. On boiling this solution, violet vapor of iodine appears. In presence of excess iodide, I_2 forms brown triiodide complex, I_3^- ion, which masks the yellow colour of the $[\text{SbI}_6^{3-}]$ complex ion,

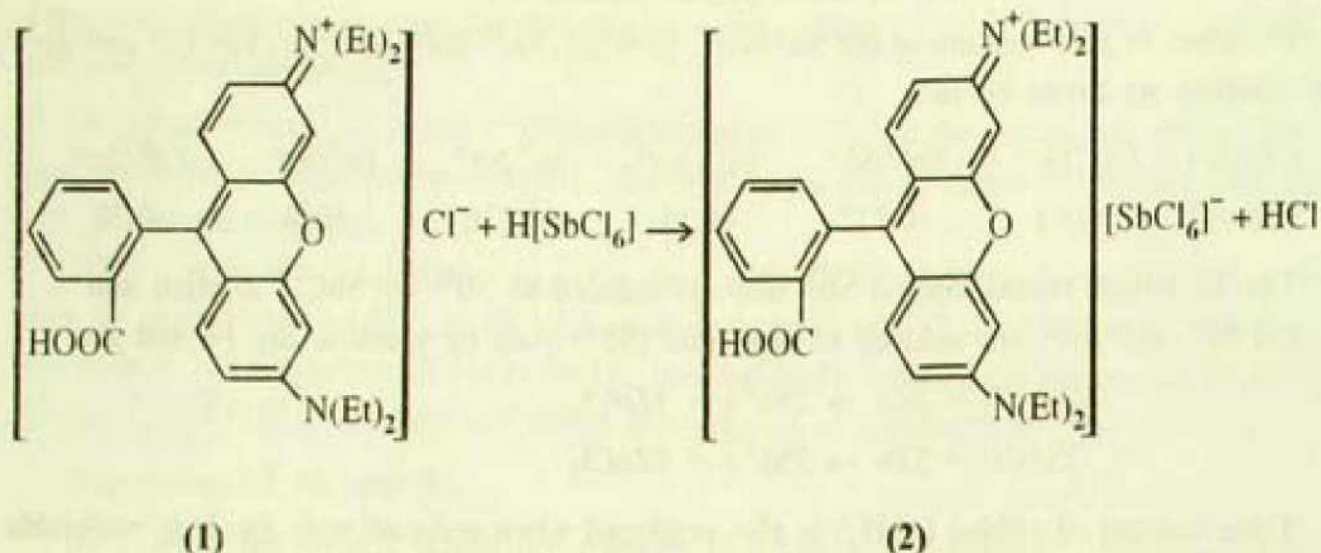


Confirmation

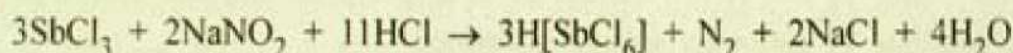
(1) Rhodamine-B test

Reagent: 0.01g of rhodamine-B in 100 ml of water.

Rhodamine B (tetraethylrhodamine) in the form of its chloride salt (1), when reacts with pentavalent antimony in strong hydrochloric acid medium, i.e., with $\text{H}[\text{SbCl}_6]$, the red colour of the dye stuff changes to violet to blue, and a finely divided precipitate of $[\text{Rhodamine-B}^+][\text{SbCl}_6^-]$ complex salt (2), having the same colour separates at once or after standing for some time.



Antimony should be present in Sb(V) state and an excess of HCl or chloride ion should be present to ensure the existence of antimony (V) as the $\text{H[SbCl}_6\text{]}$ complex. If antimony is present in trivalent Sb(III) state, as it happens on dissolution of antimony sulfides (Sb_2S_3 and Sb_2S_5) in conc.HCl, it should be oxidized to Sb(V) state with sodium or potassium nitrite in presence of conc.HCl.



Tin, which may be present as SnCl_4 under this condition, does not interfere. Small amount of iron does not interfere. Metals, forming sparingly soluble chlorides, eg., Ag^{+} , Hg_2^{2+} , Pb^{2+} etc., basic bismuth chloride, molybdates and tungstates etc., which give similar colour reactions with rhodamine-B, should be absent.

Take 1-2 drops of the test solution in a semi-micro test tube, add a few drops of conc.HCl and a little solid sodium or potassium nitrite (avoiding large excess). Warm slightly to decompose excess nitrite if any. Cool to room temperature. Now place ~1 ml of the reagent solution on a spot plate and add a drop of the oxidized test solution. The bright red colour of the reagent changes to blue-violet. Run a blank test.

Limit of identification : 0.5γ of Sb in presence of 12,500 times the amount of Sn.

Limit of dilution : 1 : 1 × 10⁶

Rhodamine-B test with Sb(III)

Sb(III) iodide may exist in aqueous solution in the form of the complex acid, $\text{H[SbI}_4\text{]}$, which is extractable in benzene. The colourless benzene extract, reacts with rhodamine-B reagent imparting a red violet colour to the benzene layer. An addition compound of SbI_3 and rhodamine-B, is believed to be responsible for this colour.

Nitrites if present, should be decomposed by boiling with urea, prior to performing this test, since NO_2^{-} ion may oxidize Sb(III) to Sb(V) and also iodide to iodine. If any other oxidizing agent is present, it should be reduced by adding small grains of sodium sulfite.

Take 1-2 drops of the test solution in a semi-micro test tube, add 5 drops of 1:3 sulfuric acid and 1 drop of 10% KI solution. Add 1 ml of benzene and shake. Transfer 1-2 drops of the benzene layer to a spot plate with the help of a capillary dropper and add 1 drop of 0.2% rhodamine-B solution. A violet colour of antimony iodide-rhodamine -B complex, diffusing into the benzene layer is observed. Run a blank test using 1:3 sulfuric acid only.

This reaction is specific for the detection of small amount of Sb.

Limit of identification: 0.2γ of Sb

Limit of dilution: 1 : 2.5×10^5

If a freshly prepared benzene solution of the reagent is used, it is possible to detect even much smaller amount of Sb, however, bismuth, mercury and gold salts and also molybdates, tungstates interfere under this condition by imparting red colour to the benzene layer.

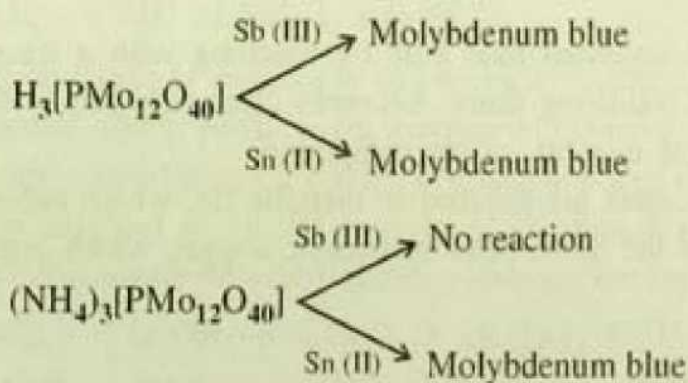
Limit of identification: 0.05γ of Sb

Limit of dilution: 1 : 1×10^6

(2) Phosphomolybdic acid ($H_3[PMo_{12}O_{40}]$) reagent

Reagent: Freshly prepared 5% aqueous solution of phosphomolybdic acid. The reagent does not keep well in solution.

Sb(III) and Sn (II) reduce phosphomolybdic acid to *molybdenum blue*, which is a mixed valent molybdenum compound of unknown composition. It is intensely blue coloured due to intervalence charge transfer transitions. In this respect, of course, Sb(III) behaves slightly different from Sn(II). While Sn(II) reduces both phosphomolybdic acid ($H_3[PMo_{12}O_{40}]$) and its ammonium salt, ammonium phosphomolybdate, $(NH_4)_3[PMo_{12}O_{40}]$, to molybdenum blue, Sb(III) reduces only phosphomolybdic acid to molybdenum blue, it is unreactive to ammonium phosphomolybdate:

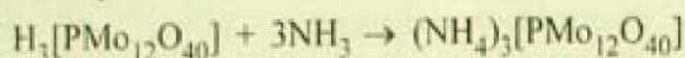


Therefore, by treating the test solution successively with phosphomolybdic acid and ammonium phosphomolybdate it is possible to identify and differentiate Sb(III) and Sn(II). However, the test is specific for antimony, if it is carried out with the solution obtained after dissolving the precipitated sulfides in conc.HCl, where antimony exists as $SbCl_3$, whereas, tin exists as $SnCl_4$, which has no effect on the reagent.

Place a drop of the phosphomolybdic acid solution on a drop reaction paper and allow the paper to dry. Now add a drop of the test solution and hold the paper in steam. A blue colouration will appear if Sb(III) or Sn(II) or both are present.

If a blue colouration is produced, repeat the test as follow:

Place a drop of the phosphomolybdic acid solution on a drop reaction paper, and hold the same for a short while over a bottle of ammonia. By this operation phosphomolybdic acid is transformed to yellow ammonium phosphomolybdate salt:



Allow the paper to dry and then add a drop of the test solution and observe:

- (i) If no blue colour appears: Sb(III) present and Sn (II) absent.
- (ii) If a blue colour appears: Sn(II) present, but presence or absence of Sb(III) can not be inferred.

Limit of identification: 0.2γ of Sb.

Limit of dilution : 1 : 2.5×10^5

4.10. Reactions of Tin (Sn^{II} , Sn^{IV})

Indications

(1) Ignition test

Mix a small amount (<0.1g) of the solid sample with 4 times its bulk of anhydrous sodium carbonate, add a small amount of powdered charcoal, place the mixture in a dry ignition tube and heat strongly on the Bunsen flame. Tin compounds, if present, are reduced to metallic tin,



White malleable globules of tin are formed, which do not mark paper (difference from lead).

(2) Borax bead test

A borax bead, which has been coloured pale blue by touching with a trace of copper compound and then heating on the oxidizing flame, becomes clear ruby-red in the reducing flame if it is touched with a minute quantity of tin compound.

In the reducing flame tin compounds are reduced to metallic tin, which reduces the pale blue coloured Cu(II) - metaborate in the borax bead to metallic copper, which imparts a ruby-red colour on the borax bead.

(3) Test by flame colour

When hydrogen gas is evolved from the reaction of zinc with hydrochloric acid in presence of traces of tin compounds, the gas produces a characteristic blue colour in the non-luminous flame of a Bunsen burner. Although the exact cause of this phenomenon is not clearly known, it is however, not due to the formation tin hydride. The flame colour is specific for tin and even minute quantity of tin can be detected by this test. Large quantity of arsenic interfere. Precipitated hydrated metastannic acid, after ignition, decisively responds to this test.

In a small beaker (25 ml) take a small amount of the solid sample or ~1 ml of the test solution, pour considerable amount (~10 ml) of conc.HCl and add a few granules of pure zinc.

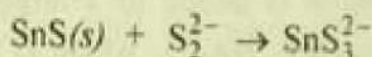
Stirr the mixture with a semi-micro test tube filled with cold water and hold the portion of the test tube dipped into the mixture in the non-luminous flame of a Bunsen burner. A characteristic blue flame mantle is formed around the test tube, which indicates the presence of very small quantity of tin.

(4) H_2S -water

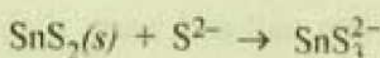
In 0.25-0.3 M hydrochloric acid medium both Sn(II) and Sn(IV) react with H_2S to form respectively brown precipitate of Sn(II) sulfide, SnS and yellow precipitate of Sn(IV) sulfide, SnS_2 .



Both the sulfides, SnS and SnS_2 , are soluble in conc. HCl (distinction from As(III) and Hg(II) sulfides). Both the precipitates dissolve in yellow ammonium sulfide or ammonium polysulfide $[(\text{NH}_4)_2\text{S}_x]$, to form thiostannate (SnS_3^{2-}) ion:



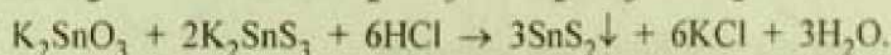
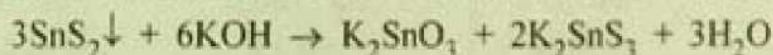
SnS_2 is also soluble in colourless ammonium sulfide, $(\text{NH}_4)_2\text{S}$, solution in which SnS is not soluble :



On acidification of the thiostannate solution, yellow precipitate of Sn (IV) sulfide, SnS_2 , appears with liberation of H_2S gas:



Tin (II) sulfide (SnS) is practically insoluble in caustic alkali, but tin(IV) sulfide (SnS_2) is soluble in caustic alkali, producing a mixture of stannate and thiostannate. For separation of Sn(II) from other metal ions by sulfide precipitation and then dissolution in caustic alkali, Sn(II) should be oxidized to Sn(IV) state by H_2O_2 , before precipitating as sulfide. Mixture of stannate and thiostannate on acidification, yields yellow precipitate of Sn(IV) sulfide, SnS_2 .

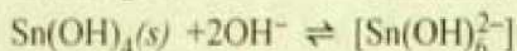
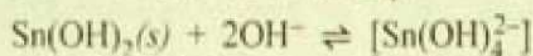
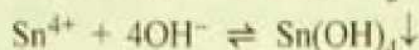
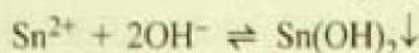


Sn (IV) may be masked by complex formation with oxalic acid. If a Sn (IV) solution containing oxalic acid is treated with H_2S water, SnS_2 is not precipitated, as Sn(IV) exists in the form of a stable oxalatocomplex, $[\text{Sn}(\text{C}_2\text{O}_4)_4(\text{H}_2\text{O})_2]^{4-}$ ion. Taking advantage of this phenomenon, Sn(IV) may be separated from arsenic and antimony by precipitation of their sulfides in HCl medium.

(5) NaOH solution (~2M)

To 1 drop of the test solution in a semi-micro test tube, add 1 drop of dilute (2M) NaOH

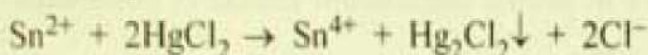
solution. White precipitate of tin (II) and, or tin (IV) hydroxides appear. The precipitates dissolve in excess of alkali, forming hydroxo complexes:



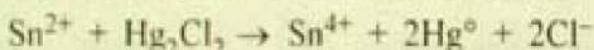
Hydroxides, Sn(OH)_2 and Sn(OH)_4 , are also precipitated by *aq-NH*₃, but the precipitates do not dissolve in excess ammonia.

(6) Mercuric chloride (HgCl_2) solution (0.05M)

Sn(II): If small amount of Sn(II) is added to a large amount of HgCl_2 solution, white precipitate of Hg_2Cl_2 is formed.



On the other hand, if a small amount of HgCl_2 solution is added to a large amount of sample solution containing Sn(II), then HgCl_2 is first reduced to Hg_2Cl_2 which is then further reduced to finely divided black metallic mercury:



Sn(IV): Does not react with HgCl_2 . Take 1-2 drops of test solution in a semi-micro test tube, add a few drops of conc.HCl and a few pieces of iron nail and warm slightly. Sn (IV) if any, is reduced to Sn(II) by this operation.



Centrifuge and add one drop of HgCl_2 solution to ~1 ml of the centrifugate. Grey to black precipitate appears if Sn^{2+} is present.

(7) Metallic Zn

When Sn(II) and Sn (IV) salts are treated with Zn metal, tin metal is separated in a spongy form which adheres to the zinc metal. The E° values of the corresponding redox couples are:

	Zn^{2+}/Zn	Fe^{2+}/Fe	$\text{Sn}^{4+}/\text{Sn}^{2+}$	Sn^{2+}/Sn
$E^\circ(\text{volt})$	-0.76	-0.44	+0.15	-0.136

The E° values indicate the feasibility this reduction.

Take a drop of the acidic test solution on a platinum foil and place a small piece of pure and clean zinc granule on the platinum foil, so that the zinc metal remains in contact with the test solution. After some time, tin is partially deposited in a spongy form upon the zinc metal, but no stain is formed on the platinum foil (distinction from antimony). Collect the precipitated spongy tin metal in a semi-micro test tube, dissolve in conc.HCl and add one drop of this solution to 1 ml of HgCl_2 solution. Grey to black precipitate of $\text{Hg}_2\text{Cl}_2/\text{Hg}$, will be formed.

(8) Lead nitrate-Bismuth nitrate-Sodium hydroxide test

Reagent:

- (i) Bismuth nitrate (0.2 M): To 50 ml water add 5 ml of conc. HNO_3 . Dissolve 9.7 g of bismuth nitrate pentahydrate $[\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}]$ in this mixture and dilute to 100 ml.
- (ii) Lead nitrate (0.25 M) : Dissolve ~8.3 g of lead nitrate $[\text{Pb}(\text{NO}_3)_2]$ in water and dilute to 100 ml.
- (iii) NaOH solution (2 M): Dissolve 8 g of NaOH in water and dilute to 100 ml.

Alkaline solution of sodium stannite (Na_2SnO_2) reduces Bi^{3+} and Pb^{2+} to finely divided black metallic states, Bi^0 and Pb^0 respectively. Reduction of Pb^{2+} is slow, but it is accelerated tremendously when small amount of Bi^{3+} is also simultaneously reduced. Bismuth (III) induces the reduction of Pb^{2+} by sodium stannite.

Place 1 drop of lead nitrate solution and then 1 drop of bismuth nitrate solution on a spot plate. Add 1-2 drops of NaOH solution (~2M).

Take 1-2 drops of the test solution in a centrifuge tube, add a few drops of conc. HCl and a few pieces of clean iron nail. Warm and centrifuge. To the centrifugate add drops of NaOH solution (~2M) until the white precipitate (due to $\text{Sn}(\text{OH})_2$) which is initially formed, just dissolves, producing a solution of sodium stannite. Centrifuge and add 1 drop of the centrifugate to the reagent mixture $[\text{Pb}(\text{NO}_3)_2, \text{Bi}(\text{NO}_3)_3 \text{ and } \text{NaOH}]$ on the spot plate. Immediate blackening is observed if tin is present.

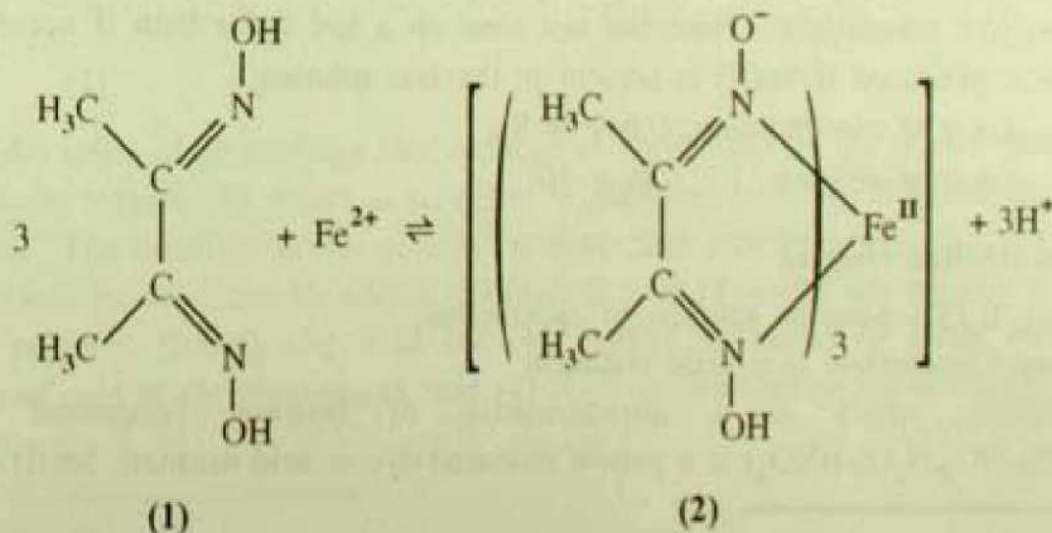
N.B: The chemical reactions have already been discussed under bismuth (*cf. p-252*).

Confirmation

(1) Dimethylglyoxime-Ferric chloride test

- Reagent:* (i) 0.1 M Ferric chloride solution in 1M HCl.
 (ii) 1% solution of dimethylglyoxime in 95% ethanol.

$\text{Fe}(\text{III})$ salts do not give any colouration when treated with dimethylglyoxime (DMGH_2 , 1) in ammoniacal medium, but $\text{Fe}(\text{II})$ salts produce a deep red colouration due to the formation *tris*-dimethylglyoximateiron(II) complex (2) under this condition.



If Sn(II) salts are present, Fe(III) is reduced to Fe(II) and a red colouration is produced with DMGH₂ - reagent in ammoniacal medium. If tin is present in Sn(IV) state it has to be reduced to Sn(II) state by the action of Al or Mg metal in presence of HCl.

Chromium, manganese, cobalt, nickel, copper, [titanium, vanadium, uranium, molybdate, tungstate]* interfere. Reducing agents which can reduce Fe(III) to Fe(II) must be absent. The test can be made specific for tin if it is performed with the conc. HCl extract of the sulfide precipitates obtained on treatment of the test solution with H₂S-water. The following procedure maybe followed to eliminate interferences by the other ions.

To 1 ml of the weakly acidic (<0.2 - 0.3M) test solution in a test tube add drops of H₂S-water to precipitate the sulfides completely. Centrifuge and discard the centrifugate. Treat the coloured precipitate of the sulfides with drops of yellow ammonium sulfide [(NH₄)₂S_x]. If a residue is left, centrifuge, discard the residue (which may be sulfides of copper group metals) and proceed with the centrifugate (which may contain the thiosalts of arsenic group metals). If no residue is left on treatment with [(NH₄)₂S_x] reagent, proceed with the whole solution. Acidify the solution with conc.HCl (test with blue litmus paper). Add a few more drops of H₂S-water to ensure complete precipitation of the sulfides. Centrifuge and discard the centrifugate. Wash the residue with water, centrifuge and completely discard the washings. Add 0.5 - 1 ml of conc.HCl to the residue, place the mixture on a hot water bath for 2-3 minutes and stir with a glass rod. Centrifuge and discard residue if any (which may be arsenic sulfide, As₂S₃ and As₂S₅). The centrifugate may contain tin as SnCl₄ (or H₂[SnCl₆]) and antimony as SbCl₃ (or H[SbCl₄]). Add a few pieces of pure Al or Mg metal to the centrifugate and warm on a hot water bath. By this operation SnCl₄ is reduced to SnCl₂, but SbCl₃ is reduced to elemental antimony, which precipitates. Cool the mixture and centrifuge. The centrifugate contains Sn(II) chloride. Call this as the prepared solution of Sn(II).

Place 3-4 drops of the prepared acidic (HCl) solution of Sn(II) in a semi-micro test tube, add 2-4 drops of 0.1 M ferric chloride solution and a few crystals of tartaric acid (to keep Fe³⁺ in solution, by preventing the precipitation of ferric hydroxide Fe(OH)₃ on addition of NH₃). Mix well and add 3 drops of DMGH₂ reagent and drops of (1 : 1) aq-NH₃ to render the solution just ammoniacal. Place the test tube on a hot water bath if necessary. A red colouration is produced if Sn(II) is present in the test solution.

Limit of identification: 0.04γ of Sn.

Limit of dilution: 1 : 1.25 × 10⁶

(2) Cacotheline reagent

Reagent: 0.25% aqueous solution of cacotheline.

Caution: Cacotheline is a toxic chemical.

Cacotheline, which is a nitroderivative of brucine, [empirical formula : C₂₁H₂₁(OH)₂NO₂.N₂O₃.HNO₃] is a yellow coloured dye in acid medium. Sn(II) salts in acid

*Rare elements

medium reduce cacotheline into a violet coloured reduction product. Other reducing agents, viz., H_2S , thiosulfate, sulfite, dithionite, Sb(III) also react with cacotheline. Coloured metallic salts, Co, Ni, Hg, Bi, As, [also Ti, V, Mo, W, U]* interfere. Although the reaction is selective for tin, but it is highly sensitive. Fe(II) salts (in the absence of fluorides and phosphate) do not react with the reagent. Therefore, a tin solution, reduced to Sn(II) with metallic iron may be used for the test. It is best to use the prepared solution of Sn(II) as described under the FeCl_3 -dimethylglyoxime test.

Place a drop of the reagent on a drop-reaction paper and add a drop of the test solution [i.e. prepared solution of Sn(II)] before the paper has dried. A violet spot surrounded by a less coloured zone appears on the yellow back ground of the reagent.

Alternatively, take 1-2 drops of the test solution [i.e. prepared solution Sn(II)] in a semi micro test tube or on a spot plate and add 1-2 drops of the reagent. A violet (purple) colouration is produced.

Note: The test is much more sensitive on a drop-reaction paper than in a test tube or spot plate.

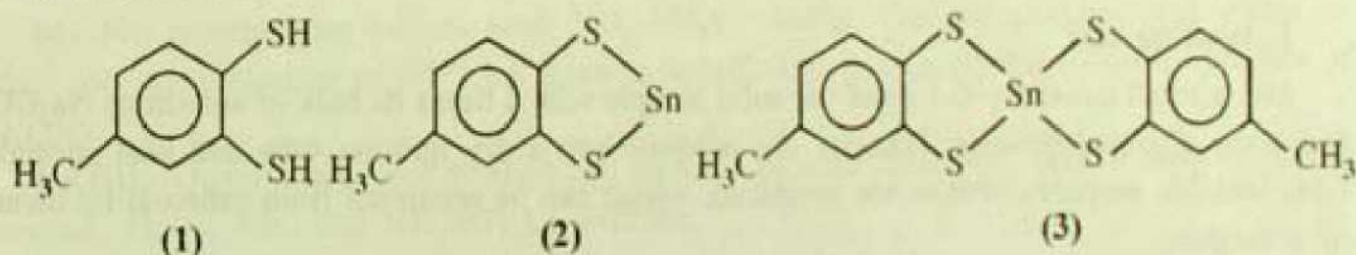
Limit of identification: 0.2 γ of Sn.

Limit of dilution: 1 : 2.5×10^5

(3) Test with dithiol reagent

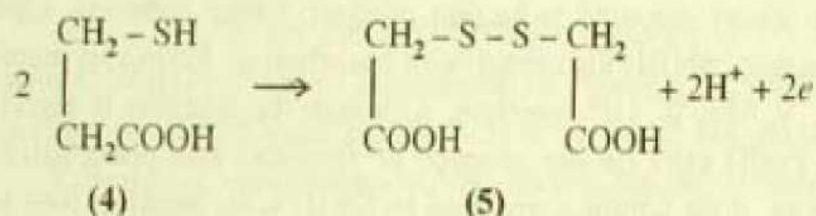
Reagent: 0.2 g of dithiol dissolved in 100 ml of 1% NaOH solution.

Alcoholic or alkaline solution of 4-methyl-1, 2-dimercaptobenzene (1), trivial name, dithiol, reacts with weakly acidic solutions of sulfide forming metal ions to form coloured precipitates. Silver, lead, mercury, cadmium, arsenic and antimony give yellow precipitates with the reagent. Copper, nickel, and cobalt form black precipitates and bismuth forms red precipitate. The reagent reacts with Sn(II) and Sn(IV) salts in strong HCl medium to give magenta coloured Sn(II) complex (2 or 3).



Sn(IV) salts, if present, are first reduced to Sn(II) state by the thiol ($-\text{SH}$) groups of the dimercaptan reagent (1) which is oxidized to the corresponding aromatic disulfide ($-\text{S}-\text{S}-$) derivative. The disulfide is not soluble in water and interferes with the test. However, the problem may be overcome by adding thioglycolic acid (4) to the test solution prior to addition of the reagent. Thioglycolic acid reduces Sn(IV) to Sn(II) or other oxidizing agents, which can oxidize the reagent (1), and (4) itself is oxidized to water soluble dithioglycolic acid (5).

*Rare elements



Take 1-2 drops of the strong hydrochloric acid test solution in a semi-micro test tube, add 1-2 drops of the dithiol reagent and place the test tube on a hot water bath. Depending upon the quantity of tin present, a red precipitate or a colouration will be produced.

If Sn (IV) is suspected, add a few drops of thioglycolic acid to the test solution prior to addition of the reagent solution.

For eliminating the interference due to the other metal ions, the test may be performed with the prepared solution of Sn(II) as described under FeCl₃- dimethylglyoxime test.

Alternatively, after dissolving the sulfide precipitates in yellow ammonium sulfide, discard the residue (Cu-group metal sulfides) and warm the centrifugate (arsenic group metal thio-salts) with an excess of 10-volume H₂O₂. This treatment ensures the formation of ammonium salts of the respective metalloacids (of As, Mo*, V*, W*) and precipitation of Sn(OH)₄ and Sb(OH)₅. Centrifuge, and discard the centrifugate. Dissolve the residue in dil.HCl and perform test with dithiol adding a few drops of thioglycolic acid before adding the reagent. If As, V*, Mo*, W* are absent, the precipitate obtained after acidification of yellow ammonium sulfide extract may be dissolved in conc.HCl and the dithiol test may be performed after adding thioglycolytic acid.

Limit of identification: 0.05γ of Sn

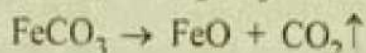
Limit of dilution: 1 : 1 × 10⁶

4.11 Reactions of Iron (Fe^{II}, Fe^{III})

Indicaiton

1. Ignition test

Mix a small amount (~0.1 g) of the solid sample with 4 times its bulk of anhydrous Na₂CO₃ and some charcoal powder. Transfer the mixture into a dry ignition tube and heat strongly. Grey metallic particles of iron are produced, which can be separated from cahrc coal by means of a magnet.



The grey metallic iron particles may be mechanically separated from the magnet and dissolved in dil.HCl. The HCl solution containing Fe(II) maybe subjected to other chemical tests.

*Rare elements

2. Borax bead test

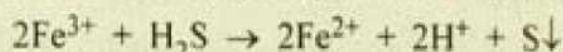
When a minute quantity of an iron compound is subjected to borax bead test, the bead turns yellow-brown when hot and yellow when cold in the oxidizing flame. With large quantities of iron the colour of the borax bead in the oxidizing flame is redish brown. If the bead is placed in the reducing flame, its colour changes to bottle green.

3. H₂S - water

To 1-2 drops of weakly acidic test solution add 1-drop of H₂S water.

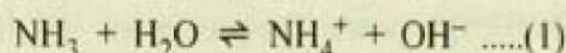
Fe(II) : No precipitation, as the solubility product of FeS is not exceeded in acid medium.

Fe(III): In acidic solution Fe³⁺ (yellow colour) is reduced by H₂S to Fe²⁺ (bottle green colour) and H₂S is oxidized with separation milky white colloidal sulfur. In neutral solution, however, initially a blueish colouration appears due to extremely small particles of colloidal sulfur, this is followed by precipitation of sulfur:



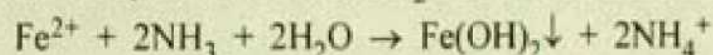
(4) Ammonia solution and NH₃-NH₄Cl buffer solution

Aqueous ammonia solution is basic,



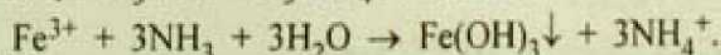
In presence of NH₄Cl, which is a completely ionized salt, [NH₄Cl → NH₄⁺ + Cl⁻], concentration of NH₄⁺ ion is high. Due to common ion effect of NH₄⁺ ion, the equilibrium (1) remains shifted to the left. As a result, the concentration of OH⁻ ion, required for precipitation of metal hydroxides is less. [pK_{sp} : Fe(OH)₂, 17; Fe(OH)₃ = 37.5 at 25°C].

Fe(II): (i) Precipitation of Fe(OH)₂ occurs on addition of aq-NH₃ solution.



(ii) No precipitation occurs with NH₃-NH₄Cl buffer. Due to common ion effect of NH₄⁺ ion, concentration of OH⁻ ion remains insufficient to exceed the solubility product of Fe(OH)₂.

Fe(III): Quantitative precipitation of brown coloured Fe(OH)₃ occurs with both the reagents, i.e., aq-NH₃ and NH₃-NH₄Cl solution.

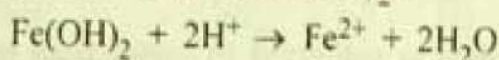
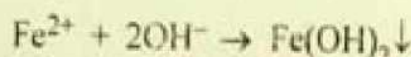


As the solubility product of Fe(OH)₃ is much less than that of Fe(OH)₂, concentration of OH⁻ ion even in presence of NH₄Cl is sufficient to exceed the solubility product of Fe(OH)₃. The precipitate dissolves on boiling with mineral acids.

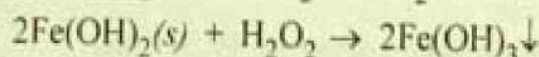
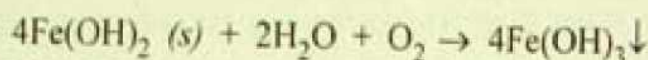
(5) NaOH solution (~2M)

To 1-2 drops of the weakly acidic test solution add drops of NaOH solution (~2 M) until alkaline.

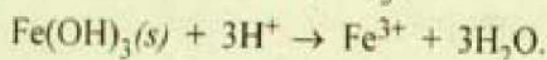
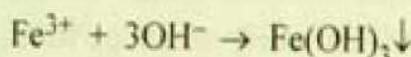
Fe(II): Greenish white precipitate of ferrous hydroxide, Fe(OH)₂, appears in absence of air. The precipitate is insoluble in excess alkali but soluble in acids.



On exposure to air, the precipitate of $\text{Fe}(\text{OH})_2$ gradually turns redish brown due to oxidation to ferric hydroxide, $\text{Fe}(\text{OH})_3$. This transformation becomes rapid if an oxidizing agent, such as, H_2O_2 is added.



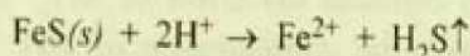
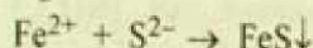
Fe(III): Redish brown precipitate of ferric hydroxide appears. The precipitate is insoluble in excess alkali (distinction from aluminium hydroxide), but soluble on boiling with mineral acid:



(6) Ammonium sulfide solution

To 1-2 drops of weakly acidic test solution on a spot plate, add 1-2 drops of ammonium sulfide solution.

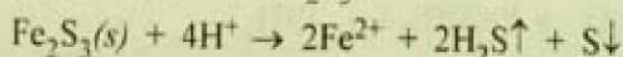
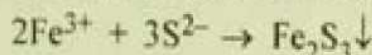
Fe(II): Black precipitate of ferrous sulfide (FeS) appears. The precipitate is soluble in acids with evolution of H_2S



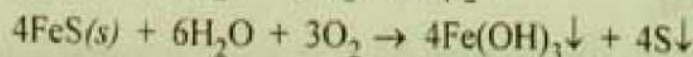
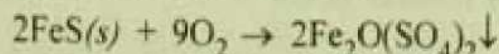
Fe(III): Black precipitate consisting of ferrous sulfide and sulfur is produced in weakly acidic solution. Fe(III) is reduced to Fe(II) *in situ* by sulfide (S^{2-}) ion, which is oxidized to form colloidal milky sulfur.



In alkaline solution, black precipitate of ferric sulfide (Fe_2S_3) is formed, which readily dissolves in HCl forming ferrous chloride, sulfur and H_2S :



Moist ferrous sulfide on exposure to air is slowly oxidized to basic ferric sulfate and brown ferric hydroxide with separation of sulfur:



CAUTION: This last reaction is highly exothermic. It may produce so much heat that if the precipitate is filtered and the filter paper with finely divided sulfur on it is allowed to dry in air, it may catch fire. Therefore, sulfide precipitates should never be thrown into the

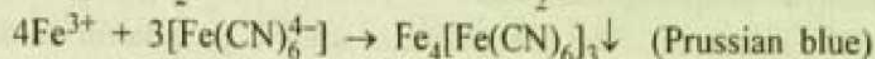
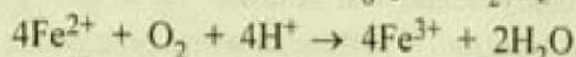
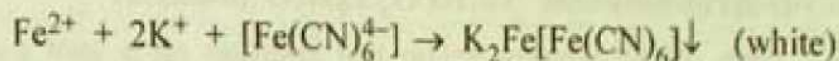


waste bin, but rather these should be washed away under running water. Only the clean filter paper should be thrown to the waste bin.

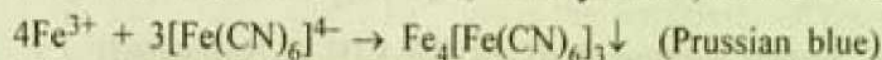
(7) Potassium ferrocyanide $K_4[Fe(CN)_6]$ solution (0.025 M)

To 1 drop of weakly acidic test solution (or, a pinch of the solid sample) on a spot plate, add 1 drop of dil.HCl and 1 drop of $K_4Fe(CN)_6$ solution and stir with a glass rod.

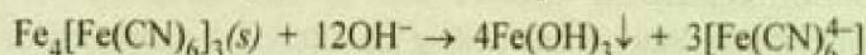
Fe(II): White precipitate of potassium iron (II) ferrocyanide, $K_2Fe[Fe(CN)_6]$ is formed in complete absence of air. Under ordinary condition, however, a pale-blue precipitate is formed, due to aerial oxidation of some Fe(II) to Fe(III), which reacts with the reagent to give Prussian blue precipitate.



Fe (III): Intense blue precipitate of iron (III) ferrocyanide (Prussian blue) is formed.



The Prussian blue precipitate is insoluble in dilute acids, but it decomposes by concentrated acids and alkali. On boiling with sodium hydroxide (~2M) solution, the blue precipitate is transformed to red-brown ferric hydroxide and ferrocyanide ion is set free:



If $FeCl_3$ solution is added to a large excess of $K_4[Fe(CN)_6]$ solution, a colloidal compound of composition $KFe[Fe(CN)_6]$, (called *soluble Prussian blue*) is formed, which can not be filtered.

Prussian blue dissolves in oxalic acid producing an intense blue solution, which may be used as an ingredient for the production of writing ink.

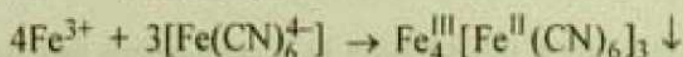
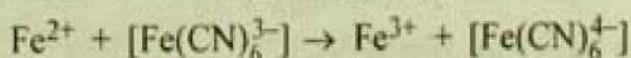
Limit of identification: 0.1γ of Fe (on paper), 0.05γ of Fe (on spot plate)

Limit of dilution: 1 : 5×10^5 (on paper), 1 : 1×10^6 (on spot plate).

8. Potassium ferricyanide $K_3[Fe(CN)_6]$ solution (0.033M)

To 1-2 drops of the weakly acidic test solution (or, a small amount of solid sample) on a spot plate, add 1 drop of dil.HCl, 1 drop of potassium ferricyanide solution and stir with a glass rod.

Fe(II): A dark blue precipitate is formed if Fe^{2+} is present. $[Fe(CN)_6]^{3-}$ ion in strong acid medium oxidizes Fe^{2+} to Fe^{3+} and itself is reduced to $[Fe(CN)_6]^{4-}$, which subsequently reacts with Fe^{3+} ion to produce the dark blue precipitate of *Turnbulls blue*, which is identical in composition as Prussian blue, $Fe_4^{III}[Fe^{II}(CN)_6]_3$.



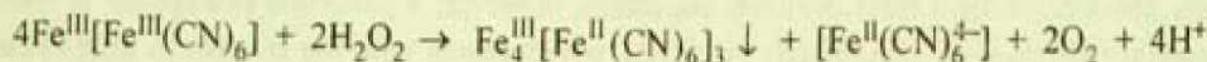
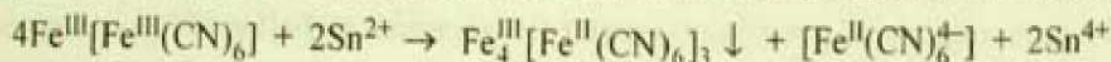
The precipitate decomposes on treatment with caustic alkali, producing red-brown precipitate of $Fe(OH)_3$ and $[Fe(CN)_6]^{4-}$ ion is set free (cf. test 7).



Fe(III): Brown colouration due to the formation of an undissociated complex, $\text{Fe}^{\text{III}}[\text{Fe}^{\text{III}}(\text{CN})_6]$.



If 1-2 drops of SnCl_2 solution or 10-volume H_2O_2 is added, the ferricyanide part of the complex is reduced to ferrocyanide and a Prussian blue precipitate is formed.



(9) Disodiumhydrogenphosphate $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (0.033M)

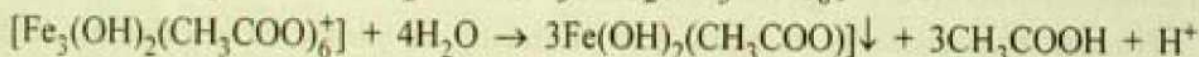
Fe(III): Place 1 drop of the weakly acidic test solution on a spot plate and add a few drops of disodiumhydrogenphosphate solution. A yellowish white precipitate of ferric phosphate is formed if Fe(III) is present. The precipitate is soluble in mineral acids:



10. Sodium acetate solution $\text{Na}(\text{OOCCH}_3) \cdot 3\text{H}_2\text{O}$ (saturated)

Fe(III): To 1 drop of the weakly acidic test solution on a spot plate add a few drops of saturated sodium acetate solution.

A redish brown colouration appears due to the formation of the complex ion $[\text{Fe}_3(\text{OH})_2(\text{CH}_3\text{COO})_6]^+$. On dilution and boiling the solution, a redish brown precipitate of basic ferric acetate is formed.



The reaction proceeds to completion in presence of excess of acetate ion, which acts as a buffer.

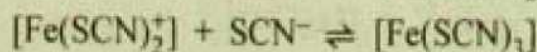
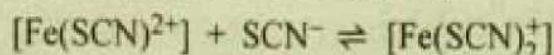
Confirmation

(1) Ammonium or potassium thiocyanate solution (0.1M)

Place one drop of the weakly acidic test solution on a spot plate and add 1 drop of the thiocyanate solution.

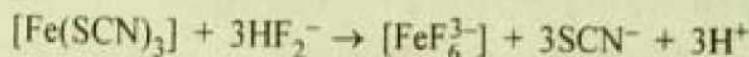
Fe(II): No colouration.

Fe(III): A blood red colouration is produced due to the formation of Fe(III) - thiocyanato complexes:



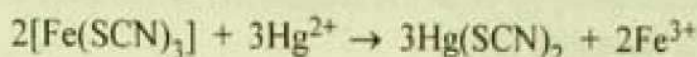
(1a) Place 1-2 drops of this blood red solution in a semi-micro test tube and add 1ml of 0.1 M HCl and 1-2 drops of isoamyl alcohol. Shake well. The amyl alcohol layer becomes red, as the neutral complex $[\text{Fe}(\text{SCN})_3]$ is extracted into the organic layer.

(1b) Place 1 drop of the blood red solution on a cavity of the spot plate and add a small crystal of ammonium or potassium hydrogen fluoride (NH_4HF_2 or KHF_2). The blood red colour is discharged due to the formation of the colourless hexafluoroferrate (III) complex ion, $[\text{FeF}_6]^{3-}$ of higher stability:



Being a hard Lewis acid, Fe^{3+} forms stronger complex with hard Lewis base, the F^- ion, than that with the soft SCN^- ion.

(1c) Place another drop of the blood red solution on another cavity of the spot plate and add 1 drop of mercuric nitrate or mercuric sulfate solution (0.01M). The blood red colour is discharged, as the soft Lewis acid, Hg^{2+} ion, snatches the soft Lewis base SCN^- ion, from its complex with hard Fe^{3+} ion,



Note

1. Coloured ions eg, Cu^{2+} , Cr^{3+} , Co^{2+} , Ni^{2+} lower the sensitivity of the test.
2. Hg^{2+} , Ag^+ ions which form soluble or insoluble salts with SCN^- ion may interfere if present in large quantities.
3. Nitrite ion (NO_2^-) forms red coloured nitrosyl thiocyanate, (NOSCN), and interferes in this test, however, this red colour disappears on heating.
4. Molybdate* forms yellow solution with SCN^- ion. On treatment with SnCl_2 , molybdate is reduced to Mo(III) , which forms a red coloured complex with SCN^- . But SnCl_2 reduces Fe^{III} to Fe^{II} which does not form red colouration with SCN^- ion.

Limit of identification: 0.25γ of Fe

Limit of dilution: 1 : 2×10^5

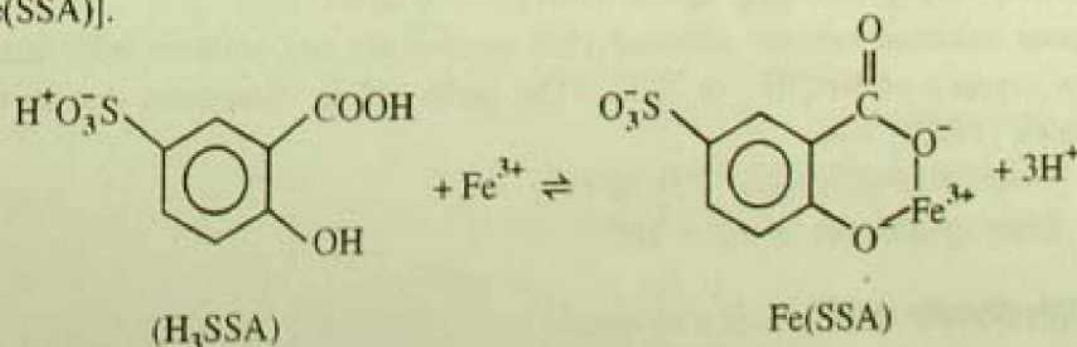
2. Sulfosalicylic acid

Reagent: 0.05 M solution in water.

Place 1 drop of the weakly acidic test solution on a spot plate and add 1 drop of the sulfosalicylic acid (H_3SSA) reagent.

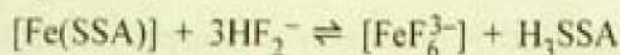
Fe(II): No colouration.

Fe(III): Violet colouration is produced due to the formation of Fe(III)-sulfosalicylate complex, $[\text{Fe}(\text{SSA})]$.



*Rare element

(2a) Add a few crystals of ammonium or potassium hydrogen fluoride to the violet solution and stir with a glass rod. The violet colour is discharged, due to the formation of more stable and colourless $[\text{FeF}_6^{3-}]$ complex,



Limit of identification: 0.5 of Fe.

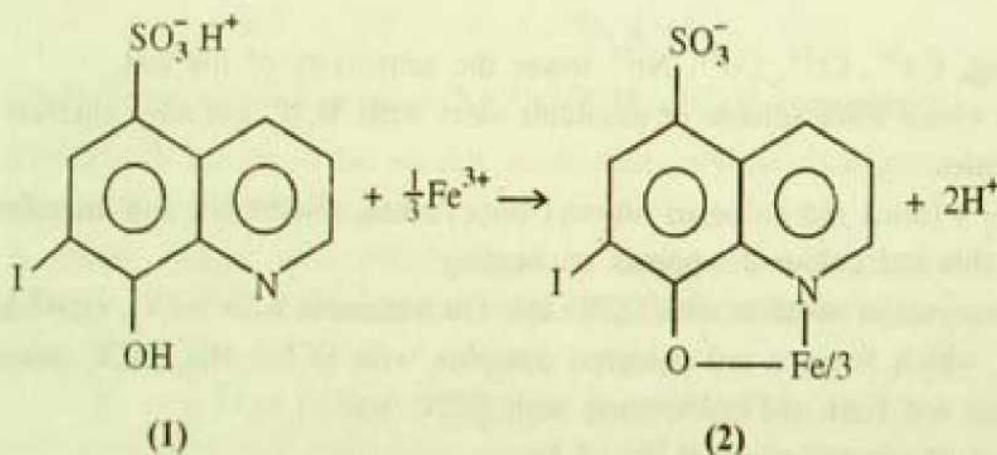
Limit of dilution: 1 : 1×10^5

3. Test with ferron (8-hydroxy -7-iodoquinoline-5-sulfonic acid)

Reagent: (0.1% solution in water).

Fe(II): No colour reaction.

Fe(III): Reacts with aqueous solution of ferron reagent (1) to produce a green colouration due to formation of the inner complex (2):



The reaction, as it appears, is pH sensitive. Optimum pH for this colour reaction is pH 2-3.5. If the test solution is strongly or less acidic, it should be neutralized or acidified as required and buffered until it shows a distinct acid reaction toward mettyl orange paper (pH=3.5).

Place 1 drop of the test solution, adjusted to pH = 3.5 (using a methyl orange paper or a pH paper) in a spot plate, add 1 drop of ferron reagent. A green colour is produced if Fe(III) is present.

Although the colour reaction is specific for Fe(III), but considerable quantities of other coloured ions interfere. Strong oxidizing agents destroy the reagent.

(3a) To the green coloured solution obtained after treating the test solution with ferron reagent, add a few crystals of NH_4HF_2 or KHF_2 . The green colour disappears due to the formation of complex $[\text{FeF}_6^{3-}]$ ion.

Limit of identification: 0.5γ of Fe

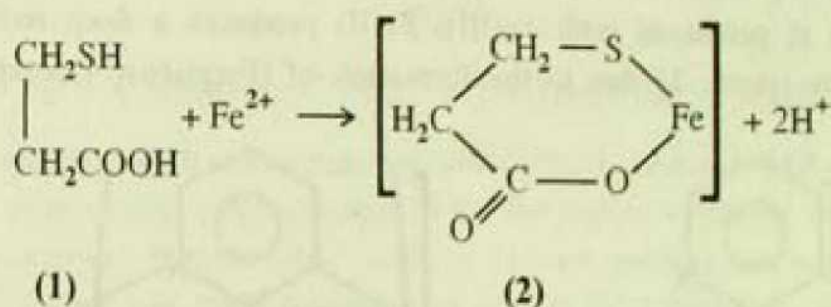
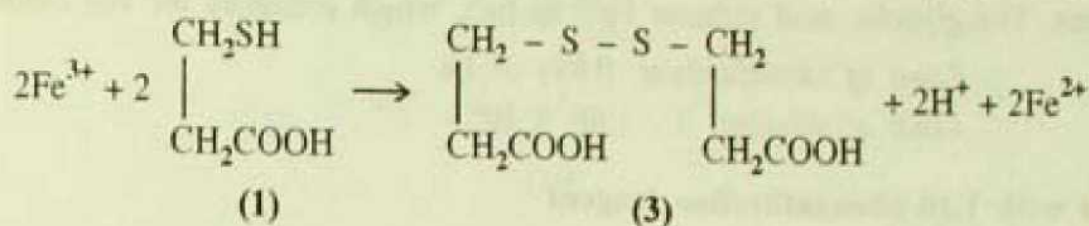
Limit of dilution: 1 : 1×10^5

4. Test with thioglycolic acid

Reagent: 1% aqueous solution.

Both Fe^{II} and Fe^{III} react with thioglycolic acid (1) in 6M ammoniacal solution to produce

purple (red-violet) coloured Fe(II) - thioglycolate complex (2). Fe(III), if present, is reduced to Fe(II) by thioglycolic acid, which is oxidized to its disulfide, dithioglycolic acid (3).

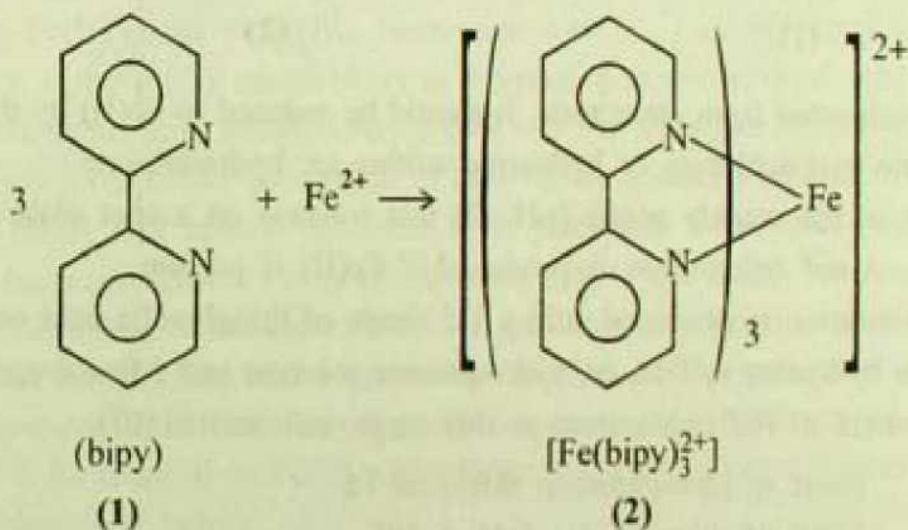


Limit of identification: 0.01γ of Fe.

5. Test with 2, 2'-bipyridine

Reagent: 2% solution of 2, 2'-bipyridine in ethanol.

In weakly acidic solution 2, 2'-bipyridine (bipy, 1) reacts with Fe(II) to form soluble and very stable deep red complex (2).



Fe(III) does not give colour reaction under this condition.

Large amount of Fe(III) imparts a yellow colour to the test solution and may mask the light red colour produced by very small amount of Fe(II) with the reagent. This problem may be over come by performing the test in presence of NH_4HF_2 or, KHF_2 , which masks Fe(III) by transforming it into $[\text{FeF}_6]^{3-}$ complex.

Place 1 drop of the weakly acidic test solution on a spot plate and add 1 drop by the bipy reagent. A red colouration is produced if Fe(II) is present.

(5a) If no red colouration appears, but the test solution is pale yellow in colour, or, if Fe(III) is suspected from other tests, add 1-2 drops of thioglycolic acid before addition of the bipy reagent. Thioglycolic acid reduces Fe^{III} to Fe^{II} , which produces the red colouration.

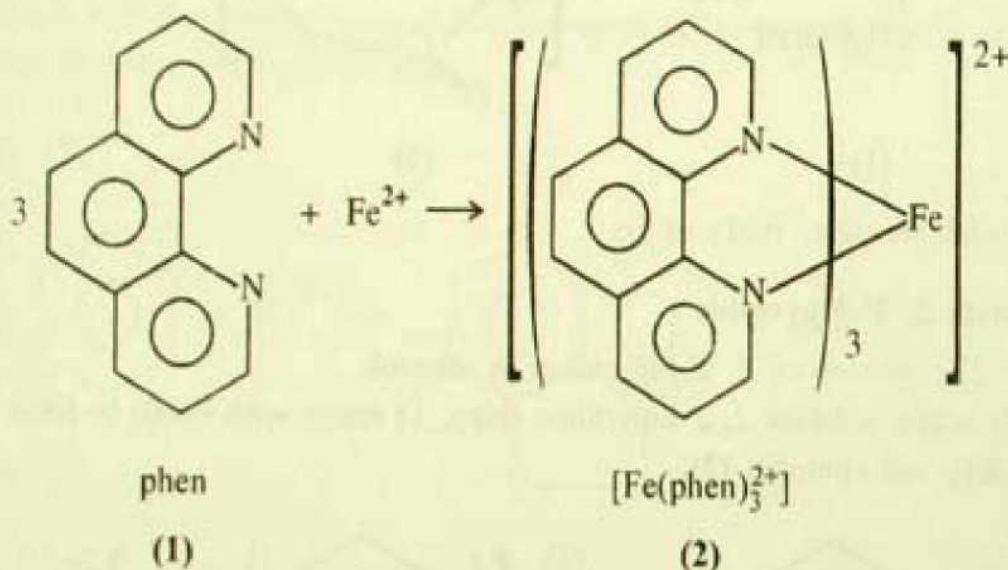
Limit of identification: 0.03γ of Fe.

Limit of dilution: 1 : 1.66×10^6

6. Test with 1,10-phenanthroline reagent

Reagent: 0.1% solution in water.

No colouration is produced with Fe(III). Fe(II) produces a deep red colouration with 1, 10-phenanthroline (phen, 1) due to the formation of $[\text{Fe}(\text{phen})_3]^{2+}$ complex (2).



If Fe(III) is suspected from other tests, it should be reduced to Fe(II) by thioglycolic acid, or, hydroxylamine hydrochloride or hydrazine sulfate or, hydroquinone.

Place 1 drop of the weakly acidic ($\text{pH} \approx 2$) test solution on a spot plate and add 1 drop of phen reagent. A red colouration is produced if Fe(II) is present.

(6a) If no coloration is produced, add a 1-2 drops of thioglycolic acid or hydroxylamine hydrochloride, or hydrazine sulfate, or, hydroquinone solution and a few drops sodium acetate solution. Appearance of red colouration at this stage indicates Fe(III).

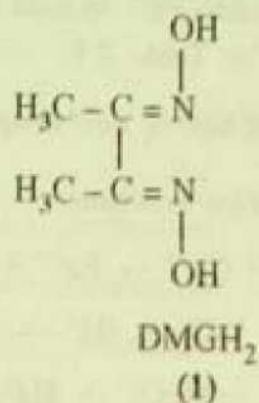
Limit of identification: 0.03γ of Fe

Limit of dilution: 1 : 1.66×10^6

7. Dimethylglyoxime (DMGH₂) reagent

Reagent: 1 % solution of DMGH₂ in ethanol.

Dimethylglyoxime (DMGH₂, 1) reacts with Fe(II) to in ammoniacal medium to produce red colouration due to the formation of probably *tris*-dimethylglyoximateiron(II) (*cf. p. 281*) $[\text{Fe}(\text{DMGH})_3]^-$ ion.



Fe(III) salts do not give such colour reaction with DMGH₂, but interfere, due to precipitation of Fe(OH)₃ in the ammoniacal medium required for the test. Interference due to Fe(III) maybe eliminated by complexing it with citric acid, or tartaric acid or ammonium or potassium bifluoride. Cobalt, nickel and large quantities of copper salts interfere, and must be absent.

Place 1 drop of the weakly acidic test solution on a spot plate, add 1 drop of DMGH₂ reagent, and a few crystals of tartaric acid, or, citric acid and then add drops of 1:1 aq-NH₃ until ammoniacal. A red colouration is produced if Fe(II) is present. A red crystalline precipitate is formed if Ni(II) is present.

7(a) DMGH₂ test for Fe in presence of Co, Ni and Cu

Take 1 ml of the test solution in a semi-micro test tube, add a few drops of 10-volume H₂O₂ to oxidize Fe(II) if any to Fe(III). Neutralize with (1:1) aq-NH₃ until a faint permanent turbidity appears. Just dissolve the turbidity in drops of dil.acetic acid and add an equal volume of sodium acetate-acetic acid buffer solution (pH ~ 4.75). Heat the mixture to boiling. Under this condition only a red brown precipitate of basic ferric acetate will appear if iron is present. Cu(II), Co(II), Ni(II) will remain in solution. If phosphate is present, only iron (III) and copper(II) will be precipitated as their phosphates, Co(II) and Ni(II) will remain in solution. Centrifuge and discard the centrifugate. Wash the residue with water by centrifugation. Dissolve the residue in hot dil.HCl and add a few pieces of pure Al foil or a pinch of pure Zn dust. If copper(II) is present,, it will be reduced and precipitated as metallic copper. If iron is present as Fe (III) it will be reduced to Fe(II). Centrifuge and use the centrifugate for DMGH₂ test of iron (II) as described before.

Limit of identification: 0.04γ of Fe²⁺

Limit of dilution: 1 : 1.25 × 10⁵

Oxidation of Fe(II) to Fe(III) and Reduction of Fe(III) to Fe(II) by common oxidants and reductants in acid medium.

For performing qualitative identification tests, it is often necessary to reduce Fe³⁺ to Fe²⁺ and to oxidize Fe²⁺ to Fe³⁺. E° value of Fe³⁺/Fe²⁺ couple (+0.77 volt in 1 M acid medium) falls almost at the middle of the stability field of water (cf. Sect 2.4), consequently Fe²⁺ may

be oxidized to Fe^{3+} and Fe^{3+} may be reduced to Fe^{2+} in acid medium by quite a good number of oxidants and reductants as summarised in Table 4.1.

Table 4.1 : Oxidation and reduction of $\text{Fe}^{\text{III}} / \text{Fe}^{\text{II}}$ couple.

<i>Oxidant couples</i>	<i>E°(volt)</i>	<i>Oxidation reactions.</i>
$\text{Ce}^{4+}/\text{Ce}^{3+}$	1.45	$\text{Fe}^{2+} + \text{Ce}^{4+} \rightarrow \text{Fe}^{3+} + \text{Ce}^{3+}$
$\text{O}_2, \text{H}^+/\text{H}_2\text{O}$	0.815	$4\text{Fe}^{2+} + \text{O}_2 + 4\text{H}^+ \rightarrow 4\text{Fe}^{3+} + 2\text{H}_2\text{O}$
$\text{KMnO}_4, \text{H}^+/\text{Mn}^{2+}$	1.51	$5\text{Fe}^{2+} + \text{MnO}_4^- + 8\text{H}^+ \rightarrow 5\text{Fe}^{3+} + \text{Mn}^{2+} + 4\text{H}_2\text{O}$
$\text{K}_2\text{Cr}_2\text{O}_7, \text{H}^+/\text{Cr}^{3+}$	1.33	$6\text{Fe}^{2+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ \rightarrow 6\text{Fe}^{3+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$
$\text{HNO}_3, \text{HCl}/\text{NOCl}$	0.94	$2\text{Fe}^{2+} + \text{HNO}_3 + 3\text{HCl} \rightarrow 2\text{Fe}^{3+} + \text{NOCl}\uparrow + 2\text{Cl}^- + 2\text{H}_2\text{O}$
$\text{NaClO}_3, \text{H}^+/\text{Cl}^-$	1.45	$6\text{Fe}^{2+} + \text{ClO}_3^- + 6\text{H}^+ \rightarrow 6\text{Fe}^{3+} + \text{Cl}^- + 3\text{H}_2\text{O}$
$\text{H}_2\text{O}_2, \text{H}^+/\text{H}_2\text{O}$	0.682	$2\text{Fe}^{2+} + \text{H}_2\text{O}_2 + 2\text{H}^+ \rightarrow 2\text{Fe}^{3+} + 2\text{H}_2\text{O}$
HNO_3/NO	0.96	$3\text{Fe}^{2+} + \text{HNO}_3 + 3\text{H}^+ \rightarrow 3\text{Fe}^{3+} + \text{NO}\uparrow + 2\text{H}_2\text{O}$
<i>Reductant couples</i>	<i>E° (volt)</i>	<i>Reduction reactions</i>
Al^{3+}/Al	- 1.67	$3\text{Fe}^{3+} + \text{Al} \rightarrow 3\text{Fe}^{2+} + \text{Al}^{3+}$
Zn^{2+}/Zn	- 0.76	$2\text{Fe}^{3+} + \text{Zn} \rightarrow 2\text{Fe}^{2+} + \text{Zn}^{2+}$
Cd^{2+}/Cd	- 0.41	$2\text{Fe}^{3+} + \text{Cd} \rightarrow 2\text{Fe}^{2+} + \text{Cd}^{2+}$
$\text{Sn}^{2+}/\text{Sn}^{4+}$	0.15	$2\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow 2\text{Fe}^{2+} + \text{Sn}^{4+}$
I^-/I_2	0.53	$\text{Fe}^{3+} + \text{I}^- \rightarrow \text{Fe}^{2+} + \frac{1}{2}\text{I}_2$
$\text{NH}_2\text{OH}/\text{N}_2\text{O}$		$4\text{Fe}^{3+} + 2\text{NH}_2\text{OH} \rightarrow 4\text{Fe}^{2+} + \text{N}_2\text{O} + \text{H}_2\text{O} + 4\text{H}^+$
$\text{N}_2\text{H}_4/\text{N}_2$		$4\text{Fe}^{3+} + \text{N}_2\text{H}_4 \rightarrow 4\text{Fe}^{2+} + \text{N}_2 + 4\text{H}^+$
$\text{C}_6\text{H}_8\text{O}_6/\text{C}_6\text{H}_6\text{O}_6^*$		$2\text{Fe}^{3+} + \text{C}_6\text{H}_8\text{O}_6 \rightarrow 2\text{Fe}^{2+} + \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+$
$\text{SO}_2, \text{H}_2\text{O}/\text{SO}_4^{2-}$	0.20	$2\text{Fe}^{3+} + \text{SO}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + \text{SO}_4^{2-} + 4\text{H}^+$
$\text{H}_2\text{S}/\text{S}\downarrow$	0.14	$2\text{Fe}^{3+} + \text{H}_2\text{S} \rightarrow 2\text{Fe}^{2+} + \text{S}\downarrow + 2\text{H}^+$

* $\text{C}_6\text{H}_8\text{O}_6$ -Ascorbic acid, $\text{C}_6\text{H}_6\text{O}_6$ - Dehydroascorbic acid: $\text{C}_6\text{H}_8\text{O}_6 \rightarrow \text{C}_6\text{H}_6\text{O}_6 + 2\text{H}^+ + 2e$

Oxidants and reductants are to be so chosen that the corresponding conjugated components do not interfere in the subsequent identifying tests by forming a coloured solution, or by reacting with the reagent. Excess oxidant or reductant should be easily removable from the test solution by filtration, centrifugation or boiling. Some distinguishing tests of Fe^{II} and Fe^{III} are summarised in Table 4.2.

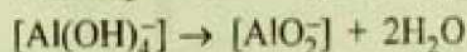
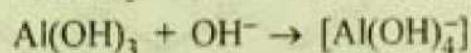
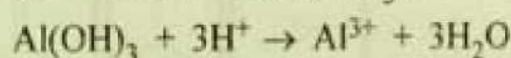
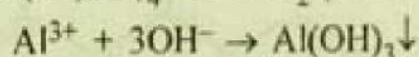
Table 4.2 Distintive tests of Fe^{II} and Fe^{III} ions

Reagents	Fe^{II}	Fe^{III}
1. $\text{K}_3[\text{Fe}(\text{CN})_6]$	Deep blue precipitate	No precipitate Brown colouration
2. 2, 2'-Bipyridine	Red colouration	No reaction
3. 1,10-Phenanthroline	Red colouration	No reaction
4. Dimethylglyoxime, NH_3	Red colouration	No reaction
5. $\text{K}_4[\text{Fe}(\text{CN})_6]$	White or pale blue precipitate	Deep blue precipitate (Prussian blue)
6. $\text{NH}_4\text{SCN}/\text{KSCN}$	No reaction	Blood red colouration
7. Ag-NH_3	White to greenish precipitate	Redish-brown precipitate
8. 5-Sulfosalicylic acid	No charactenstic colouration	Violet colouration
9. Ferron	No characteristic colouration	Grenish-blue colouration

4.12 Reactions of Aluminium (Al^{III})

Indication

No characteristic test is recommendable on dry sample. NaOH extract of the sample is most suitable for testing aluminium. Aluminium oxide being amphoteric, when aluminium salts react with caustic alkali, initially aluminium hydroxide, $\text{Al}(\text{OH})_3$ is precipitated. The $\text{Al}(\text{OH})_3$ precipitate dissolves in mineral acids to form aluminium salts and dissolves in excess alkali to form aluminate ($\text{Al}(\text{OH})_4^-$ or AlO_2^-) salts (*cf. p-94*).



Metal ions, such as Fe^{III} , Cr^{III} , Hg^{II} , Cu^{II} , Cd^{II} , Fe^{II} , Mn^{II} , Co^{II} , Ni^{II} , U^{VI} * form sparingly soluble hydroxides or oxides, which once precipitated, do not dissolve in excess alkali. Pb , Zn , As , Sb , Sn , [also V , Mo , W]* are amphoteric, oxides and hydroxides of which dissolve in acids and also pass into the NaOH extract. If phosphate is present, alkaline earth metal ions (Be^{2+} *, Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+}) are precipitated as their phosphates. Metals which form sparingly soluble hydroxides, are all precipitated as phosphates on NaOH treatment. If the NaOH extract is treated with barium chloride solution, phosphate is almost completely precipitated

*Rare elements

as barium phosphate. Ba^{2+} ion, if any, does not interfere with aluminium tests. Ba^{2+} ion can easily be removed as sparingly soluble BaSO_4 on treating the solution with $\text{dil.H}_2\text{SO}_4$.

The following procedure is recommended for extraction of aluminium as aluminate, free from other metals.

Digest ~ 0.2 g of the solid sample with ~ 2 ml of $1M$ NaOH or KOH solution for 2-3 minutes. Allow the reaction mixture to stand for some time and to the clear supernatant liquid add 1 drop of BaCl_2 solution ($\sim 0.25M$). If a precipitate is formed, add more BaCl_2 solution to complete the precipitation of barium-phosphate, arsenate [molybdate, vanadate tungstate]* etc. Centrifuge and discard the residue. Acidify the clear centrifugate with $\text{dil.H}_2\text{SO}_4$, and remove the precipitate of BaSO_4 by centrifugation. Add drops of aqueous NH_3 to the centrifugate until ammoniacal. Gelatinous precipitate appears if aluminium is present. Wash the precipitate with water by repeated centrifugation to free it from ammonia (i.e., alkali). Use this neutral Al(OH)_3 precipitate directly, or, dissolve it in dilute acetic acid and use this solution for testing aluminium.

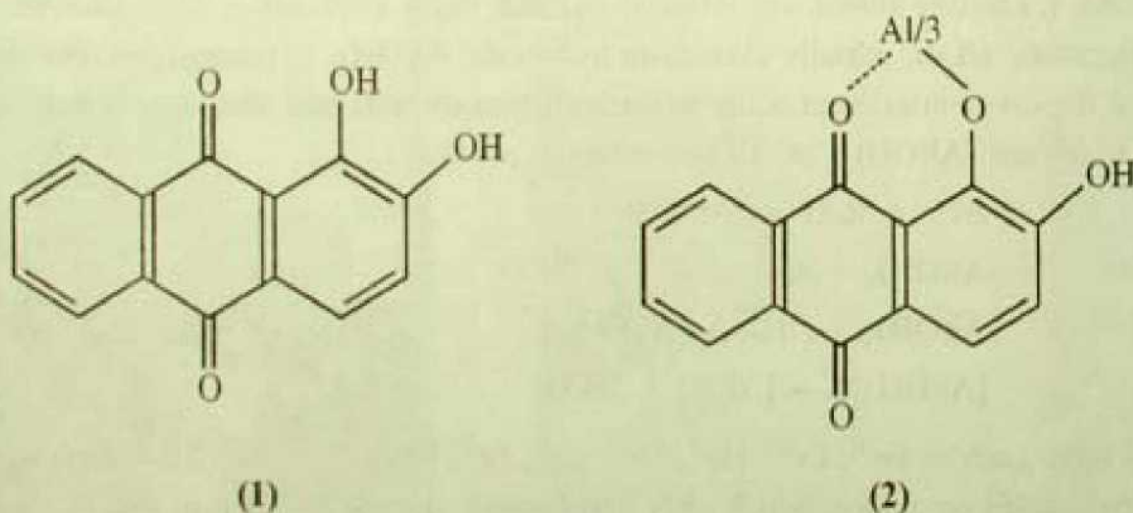
Confirmation

(1) Alizarin reagent

Reagent solution: Saturated solution of the dye stuff in 95% ethanol.

Reagent paper: Quantitative (Whatman No. 1) filter paper soaked in the reagent solution, dried and preserved in a stoppered container.

Alizarin (1) (1, 2-dihydroxyanthraquinone), forms a red lake (2) with neutral aluminium hydroxide.



Place a drop of the test solution on a drop-reaction paper impregnated with the reagent (i.e., reagent paper) and hold the paper over ammonia vapour until a violet colour (due to ammonium alizarinate) appears. If large excess of aluminium is present, the colour is visible almost immediately. Dry the violet paper at $\sim 100^\circ\text{C}$ by placing it on a watch glass covering a beaker containing boiling water. By this operation violet colour of ammonium alizarinate

*Rare elements

disappears due to its conversion to NH_3 and alizarin and the red colour of the Al-alizarin lake (2) becomes clearly visible.

Alternatively, take a small quantity of alkali free aluminium hydroxide precipitate in a semi-micro test tube and add 1 drop of the alizarin reagent. Place the test tube in a hot water bath or in a beaker containing boiling water. Beautiful red coloured Al-alizarin lake is formed within a few minutes.

Metals ions that form sparingly soluble compounds in ammoniacal medium, eg, those derived from iron, manganese, chromium, [titanium, thorium, uranium]* interfere. But their interference can be eliminated by treating the weakly acidic test solution with potassium ferrocyanide, which forms insoluble precipitate with the interfering metal ions and fix them on the drop reaction paper, whereas, aluminium ions, if present, diffuse beyond the central spot as a damp ring. If a drop of the reagent solution is added on this spot using a capillary dropper and the paper is exposed to ammonia vapour and then dried as before, a red ring of the Al-alizarin lake is formed round the central spot of the precipitates. Uranium*, if present, forms a brown precipitate with ferrocyanide. Because of its slimy nature, the uranium ferrocyanide precipitate tends to spread outwards from the spot and may obscure the Al-lake. This difficulty is over come by dipping the paper for a few minutes after treatment with the alizarin reagent into an ammonium carbonate solution, which dissolves the uranium ferrocyanide. Upon drying the paper as before, the red ring of Al-alizarin lake becomes clearly visible.

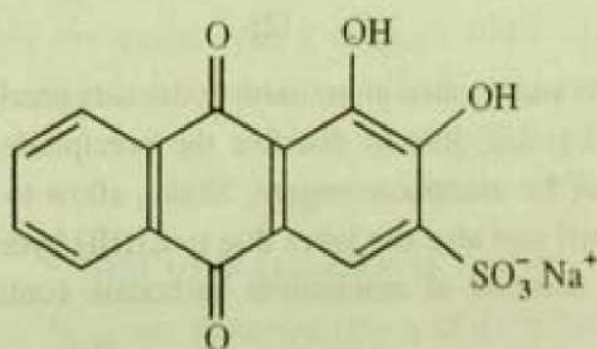
Limit of identification: 0.15% of Al

Limit of dilution: $1 : 3.33 \times 10^5$

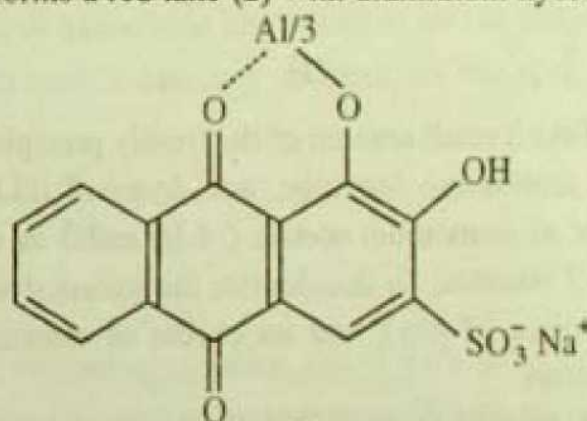
(2) Alizarin-S reagent

Reagent: 0.1% solution of alizarin-S in water.

Alizarin-S or alizarin-red-S is the sodium salt of 1, 2-dihydroxy anthraquinone-3-sulfonic acid (1) or, simply sodium alizarin sulfonate. It forms a red lake (2) with aluminium hydroxide.



(1)



(2)

The red lake is fairly stable to dilute acetic acid.

Place a drop of the dil.(1M) NaOH extract of the sample on a spot plate, add a drop of the alizarin-S reagent and then drops of dilute acetic acid until the violet colour disappears and then add 1 drop of acetic acid in excess. A red precipitate or colouration appears if aluminium is present.

Alternatively, add 1 drop of the reagent to the neutral gelatinous precipitate of $\text{Al}(\text{OH})_3$ taken in a test tube and place the test tube in a hot water bath for a few minutes. The precipitate assumes a beautiful red colour. Run a blank test.

Although salts of Ca, Sr, Ba, Fe, Co, Cu, Zn, [Ti, Zr, Ce, Th, U, Be, Lanthanides]* interfere, but they may be rendered harmless by NaOH extraction and subsequent treatment described before.

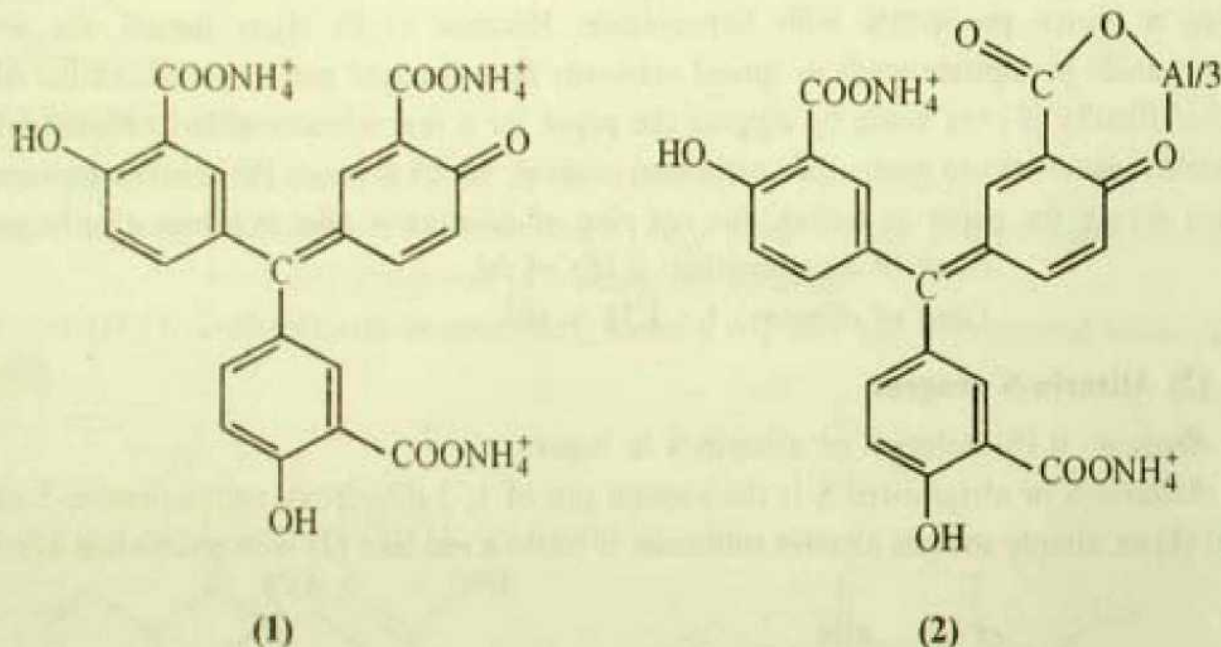
Limit of identification: 0.65 γ of Al

Limit of dilution: 1 : 7.7×10^4

3. Test with aluminon reagent

Reagent: Dissolve 0.1 g of aluminon reagent in 100 ml of water.

Aluminon (1) is triammonium aurine tricarboxylate. The reagent is adsorbed by $\text{Al}(\text{OH})_3$ precipitate giving a bright-red lake (2)



Take a small amount of the freshly precipitated and washed aluminium hydroxide precipitate in a semi-micro test tube, add drops of dil.HCl (~2M) just to dissolve the precipitate. Add ~1 ml of ammonium acetate (~6M) and 2 ml of the aluminon reagent. Shake, allow to stand for ~5 minutes. To decolourise the excess dye stuff and also the lakes due to Cr(III) hydroxide and silica (if any), add an excess of saturated solution of ammonium carbonate containing ammonia.

A bright red precipitate or colouration persists in the ammoniacal solution if aluminium is present. Run a blank test.

Iron interferes, but it is rendered harmless if the test is carried out with the NaOH (1M) extract of the sample as described before.

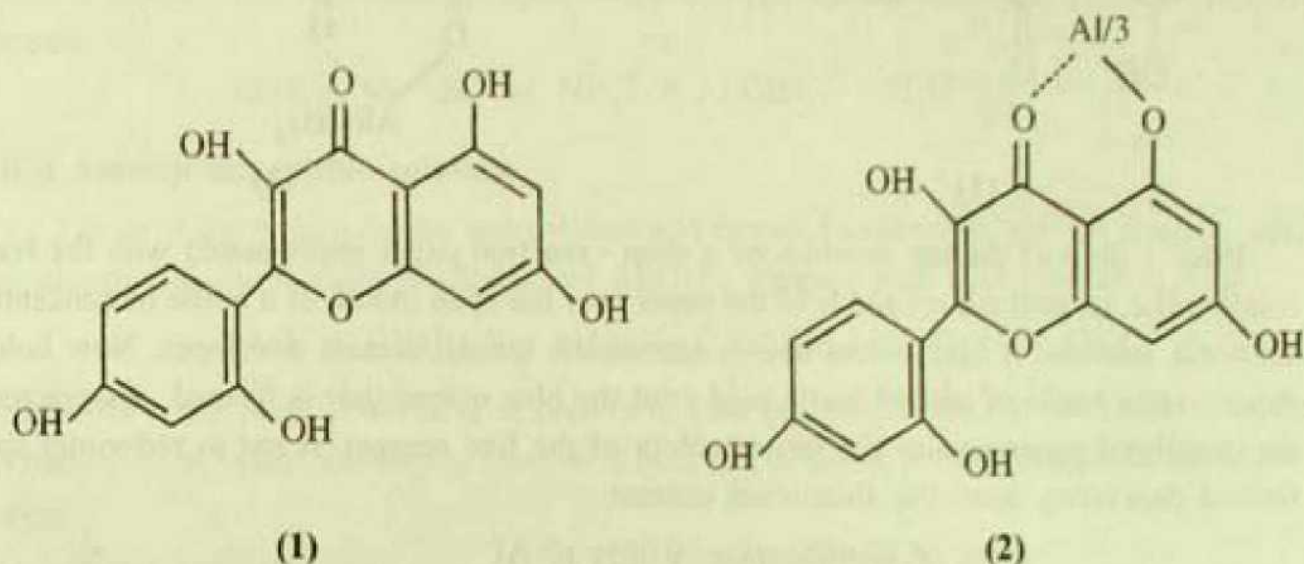
Limit of identification : 0.16 γ of Al.

*Rare elements

4. Test with morin reagent

Reagent: Saturated solution of the dye stuff in methanol.

Morin is the colouring matter of fustic. Chemically it is 3, 5, 7, 2', 4'-pentahydroxyflavanol (1). Alcoholic solution of the reagent reacts with neutral or acetic acid solution of aluminium salts to give an intense green fluorescence, both in day light and under ultraviolet radiation, due to the formation of colloiddally dispersed adsorption product (2) with Al^{3+} .



[Be, In, Ga, Sc, Zr and Th]* salts also give fluorescence with morin reagent. Except with Zr^{IV} , reaction of morin with all other metal ions are pH sensitive. Interference due to these metals are eliminated if the test is carried out with the NaOH (1 M) extract of the sample as described.

Impregnate a drop-reaction paper (Whatman No. 1) with morin reagent solution and allow the paper to dry. Place a drop of the neutral or acetic acid test solution on the reagent paper and dry again. Add a drop of dil.HCl (2M) with a capillary dropper on the spot. A green fluorescence is observed if Al^{3+} is present.

Limit of identification: 0.2γ of Al

Limit of dilution: 1 : 2.5×10^5

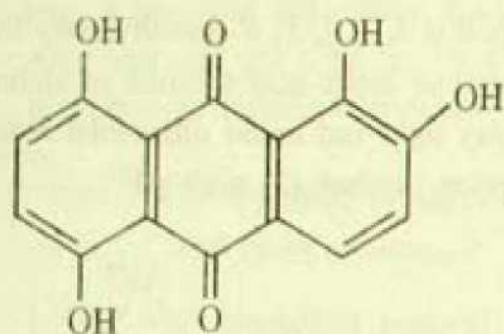
5. Test with quinalizarin reagent

Reagent: Dissolve 10 mg of quinalizarin in 2 ml of pyridine, dilute with 20 ml of acetone.

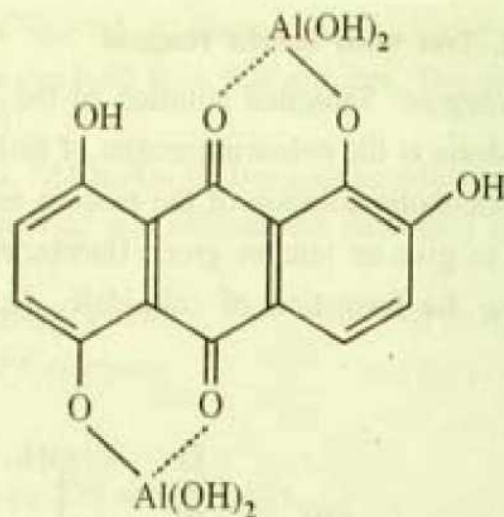
The reagent paper may be prepared by soaking quantitative (Whatman no. 1) filter paper in this solution.

Quinalizarin is 1, 2, 5, 8 - tetrahydroxyanthraquinone (1). It forms red precipitate or colouration with aluminium in neutral, or, ammonium acetate-acetic acid buffer medium due to the formation lake (2).

*Rare elements



(1)



(2)

Place 1 drop of the test solution on a drop - reaction paper impregnated with the reagent solution (i.e, reagent paper) and hold the paper over the open mouth of a bottle of concentrated ammonia solution. A blue colour due to ammonium quinalizarinate develops. Now hold the paper over a bottle of glacial acetic acid until the blue colour that is formed, disappears and the unmoisted paper regains the brown colour of the free reagent. A red to red-violet spot is formed depending upon the aluminium content.

Limit of identification: 0.005γ of Al

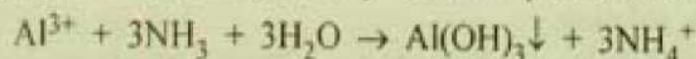
Limit of dilution: 1 : 2 × 10⁶

*Be²⁺ also forms lake with quinalizarin. In ammoniacal medium or in caustic alkaline solution a blue-violet colouration or precipitate appears depending upon Be²⁺ content. Mg²⁺ gives a corn flower blue precipitate or colouration with alkaline solution of quinalizarin, but does not interfere with aluminium, since aluminium remains as aluminate (AlO₂⁻) in alkaline solution and does not form lake with quinalizarin under this condition. Al-quinalizarin lake is formed in ammonium acetate-acetic acid medium (pH ~4.5). Interference due to most metal ions are eliminated if the test for Al is carried out with the NaOH extract of the sample after treatment with BaCl₂ solution and dil.H₂SO₄ as described before.

Other reactions of Al³⁺

(i) Ammonia solution

To 1 drop of weakly acidic test solution add drops of (1 : 1) aq-NH₃. Gelatinous white precipitate of aluminium hydroxide Al(OH)₃ is formed. The precipitate is slightly soluble in excess of the reagent, but solubility is depressed in presence of ammonium salts:



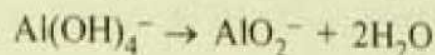
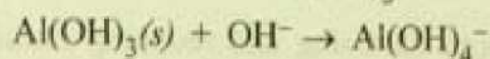
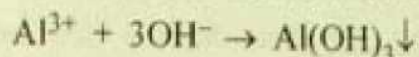
(ii) Sodium hydroxide solution

To 1 drop of the weakly acidic test solution in a semi-micro test tube, add drops of dilute

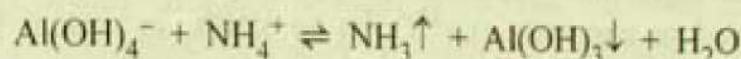
*Rare element



(1M) NaOH solution. A white gelatinous precipitate of Al(OH)_3 first appears, but dissolves in excess of the reagent, due to the formation of soluble salt, sodium aluminate:

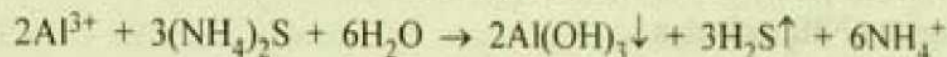


Add a few crystals of ammonium chloride to the clear, alkaline solution of sodium aluminate and boil for some times. Ammonia gas is evolved and the gelatinous white precipitate of Al(OH)_3 reappears.



(iii) Ammonium sulfide solution

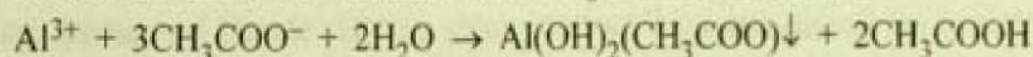
To 2 drop of the weakly acidic test solution add drops of ammonium sulfide solution until ammoniacal. Gelatinous white precipitate of Al(OH)_3 appears with evolution of H_2S gas.



Since Al^{3+} is a hard Lewis acid, it prefers to bind the hard base OH^- ion rather than the soft base S^{2-} ion, when allowed to react with both the bases, as present in ammonium sulfide solution.

(iv) Sodium acetate solution

To 1 drop of the weakly acidic test solution add 1 drop of sodium acetate solution (saturated). No precipitate is formed in neutral and cold solution. Add a few more drops of the acetate solution and boil. Voluminous precipitate of basic aluminium acetate appears, as hydrolysis of acetate ion produces OH^- ions and undissociated CH_3COOH molecules.

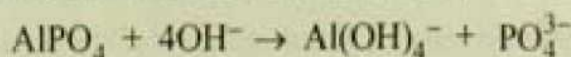


(v) Disodium hydrogenphosphate (0.03M)

To 1 drop of the weakly acidic test solution add a few drops of Na_2HPO_4 solution. White precipitate of aluminium phosphate appears.



As the reaction is reversible, the precipitate is soluble in dilute mineral acid. The precipitate also dissolves in NaOH solution due to the formation of sodium aluminate (distinction from Mg, Ca, Sr, Ba phosphates which are insoluble)



The precipitate of AlPO_4 is insoluble in acetic acid (distinction from Mg, Sr, Ba phosphates, which are soluble).

4.13 Reactions of Chromium (Cr^{III} , $\text{Cr}^{\text{VI}}\text{O}_4^{2-}$, $\text{Cr}_2^{\text{VI}}\text{O}_7^{2-}$)

Indication

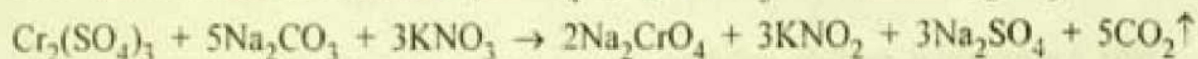
(1) Borax bead test

Green coloured bead is formed in both oxidizing and reducing flames.

(2) Oxidative fusion test

Prepare a bead of anhydrous Na_2CO_3 on a clean platinum wire loop. Dissolve a crystal of KNO_3 in the molten Na_2CO_3 bead. Touch a grain of the sample with the bead and heat the mixture in the oxidizing flame. A yellow bead results if chromium is present.

Cr^{III} salts are oxidized to chromate ($\text{Cr}^{\text{VI}}\text{O}_4^{2-}$) by KNO_3 in molten Na_2CO_3 medium.

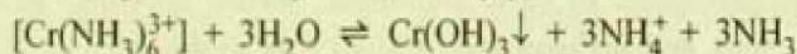
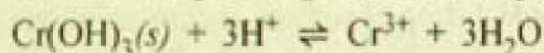
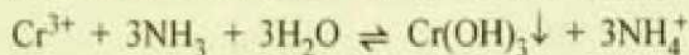


The test may also be carried out on a mica foil or on a nickel crucible-lid.

Reactions of chromium (III) salts in solution

(1) Aqueous- NH_3 solution

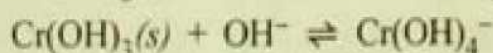
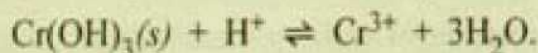
$\text{Cr}(\text{III})$ salts react with aqueous NH_3 to form grey-green precipitate of $\text{Cr}(\text{III})$ - hydroxide, $\text{Cr}(\text{OH})_3$, which dissolves in dilute mineral acids. $\text{Cr}(\text{OH})_3$ is also soluble excess of conc. NH_3 producing a violet to pink solution due to the formation of $\text{Cr}(\text{III})$ - ammine complexes. $\text{Cr}(\text{OH})_3$ is reprecipitated on boiling the $\text{Cr}(\text{III})$ -ammine complex solution.



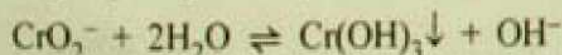
Therefore, precipitation of $\text{Cr}(\text{OH})_3$ with *aq*- NH_3 should be carried out in boiling solution and excess of NH_3 should be avoided.

(2) Sodium hydroxide solution

Grey-green gelatinous precipitate of $\text{Cr}(\text{OH})_3$ appears on addition of NaOH solution (2*M*) to Cr^{III} salt solution. Like aluminium hydroxide, Cr^{III} -hydroxide is also amphoteric as it dissolves both in mineral acid to form Cr^{III} salts and also in excess alkali to produce green solution of tetrahydroxochromite (III):



The chromite (CrO_2^-) solution upon boiling, undergoes hydrolysis and $\text{Cr}(\text{OH})_3$ is almost quantitatively reprecipitated (distinction from aluminium)





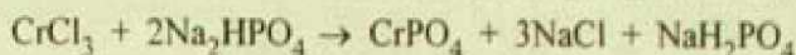
(3) Sodium carbonate solution

Sodium carbonate solution is alkaline due to hydrolysis of CO_3^{2-} ion. When Cr^{III} -salt solution is treated with sodium carbonate solution, $\text{Cr}(\text{OH})_3$ is precipitated with evolution of CO_2 ,



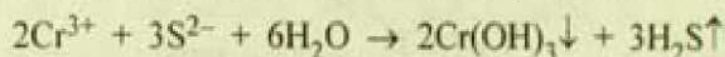
(4) Disodium hydrogenphosphate solution

Solutions of Cr^{III} salts on treatment with Na_2HPO_4 solution produce green precipitate of CrPO_4 , which is soluble in dilute mineral acids, but insoluble in cold dilute acetic acid.



(5) Ammonium sulfide solution

$\text{Cr}(\text{III})$ being a hard Lewis acid, does not prefer to bind soft Lewis base like S^{2-} ion, rather, it strongly binds the hard OH^- ion. As a result, $\text{Cr}(\text{III})$ hydroxide is precipitated with evolution of H_2S , when $\text{Cr}(\text{III})$ salts are treated with ammonium sulfide solution in water:

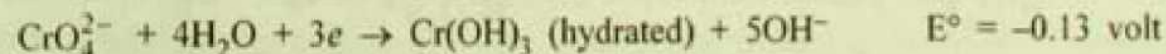


(6) Oxidation of $\text{Cr}(\text{III})$ salts to chromate/dichromate

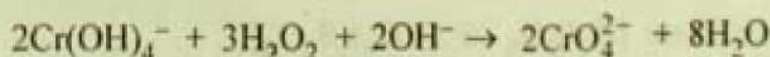
$\text{Cr}(\text{III})$ salts may be oxidized to $\text{Cr}(\text{VI})$ state, i.e., chromate (CrO_4^{2-}) /dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in the following ways:

(i) Oxidation by H_2O_2 – NaOH

When $\text{Cr}(\text{III})$ salt solution is treated with caustic alkali (NaOH/KOH), initially grey-green precipitate of $\text{Cr}(\text{OH})_3$ appears. The precipitate dissolves on boiling with excess alkali, producing a green solution of tetrahydroxo chromite, $\text{Cr}(\text{OH})_4^-$ ion, which on treatment with '20-volume' H_2O_2 , is irreversibly oxidized to form yellow coloured chromate CrO_4^{2-} ion, as the E° values in alkaline medium imply:



The net reaction may be represented according to,



(ii) Oxidation by sodium perborate ($\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$)

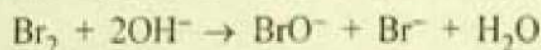
Instead of using H_2O_2 directly, it can be generated *in situ* from alkaline hydrolysis of sodium perborate,



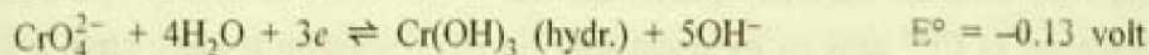
The alkaline solution of tetrahydroxo chromite $\text{Cr}(\text{OH})_4^-$ is oxidized to chromate on boiling with sodium perborate.

(iii) Oxidation by Br₂-alkali

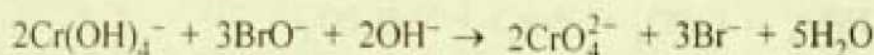
In dilute alkaline medium, bromine (Br₂) undergoes disproportionation to produce hypobromite (OBr⁻) and bromide (Br⁻) ions:



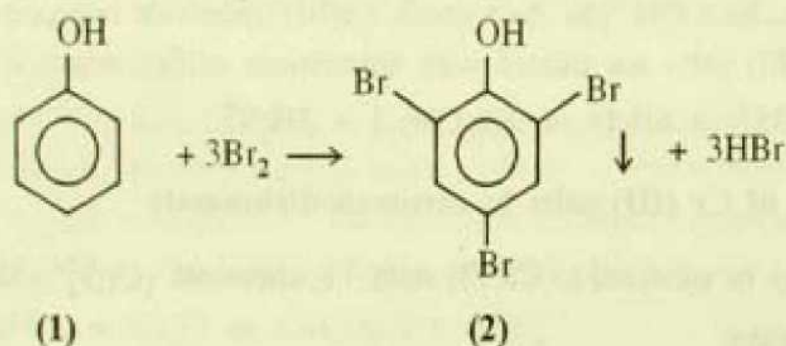
Hypobromite ion in alkaline medium oxidizes Cr(III) to chromate, as the E° values imply:



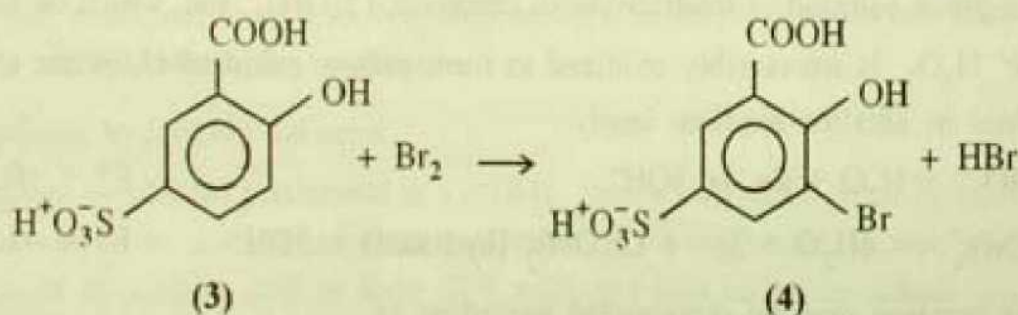
The net redox reaction is,



Excess bromine, if any may be destroyed by adding drops of phenol (1), which forms white crystalline precipitate of 2, 4, 6 tribromophenol (2) with Br₂.

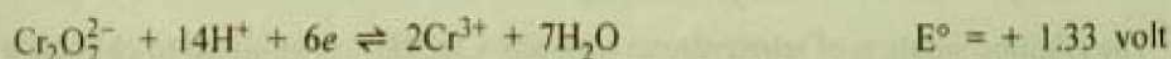


The precipitate of tribromophenol does not interfere with the tests of CrO₄²⁻ ion. The precipitate may also be removed by centrifugation. Free Br₂ can also be destroyed by adding sulfosalicylic acid (3) which is brominated to its mono-bromo derivative (4) that is soluble.



(iv) Oxidation by peroxodisulfate [K₂S₂O₈ or (NH₄)₂S₂O₈]

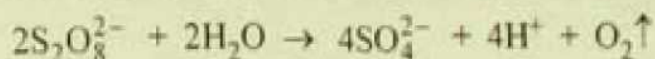
In dil.H₂SO₄ (2N - 3N) medium Cr(III) is oxidized to dichromate (Cr₂O₇²⁻) by peroxodisulfate (S₂O₈²⁻) ion as the E° values imply:



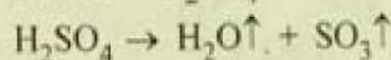
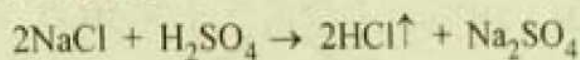
The net reaction is,



The reaction is catalysed by small amount of Ag^+ ion. The excess peroxodisulfate should be decomposed before applying the tests for $\text{Cr}_2\text{O}_7^{2-}$. Peroxodisulfate may be decomposed by boiling:



After cooling to room temperature, the solution has to be appropriately diluted for carrying out the test for chromium. Halides must be absent. Halides if present, must be removed by heating the solid sample in a **FUME CUPBOARD** with conc. H_2SO_4 until the dense white fume of sulfur trioxide is visible:



Take 1 ml of the weakly acidic test solution in a test tube, add 1 ml of 4N H_2SO_4 , 1-2 drops of silver nitrate solution (0.1 M) and heat to boiling. Add a few crystals of $\text{K}_2\text{S}_2\text{O}_8$ (or, $(\text{NH}_4)_2\text{S}_2\text{O}_8$) to the hot solution. An orange yellow colour develops. Continue boiling for some time, until the effervescence due to O_2 evolution ceases. Cool to room temperature, dilute and test for $\text{Cr}_2\text{O}_7^{2-}$.

Confirmation

If chromium is indicated in the borax bead test and in the oxidative fusion test, it is convenient to confirm it by testing in the form of chromate (CrO_4^{2-}) ion. The yellow residue left in oxidative fusion test may be treated as follows:

Extract the yellow residue left after oxidative fusion test with minimum volume of water, centrifuge and use the centrifugate for chromate testing.

If the oxidative fusion test is carried out on a sodium carbonate bead on a platinum wire loop, treat the yellow bead with drops of water on a spot plate and separate the clear extract using a capillary tube putting a piece of cotton wool on the extract to facilitate filtration (cf. Fig 3.19a). Place drops of the yellow extract on the adjacent cavities of the spot plate and perform the following tests.

(1) Barium chloride/Barium nitrate solution

Place on drop of the yellow oxidative-fusion extract on a spot plate, add drops of dil. acetic acid until acidic and finally add 1 drop of barium chloride/or, barium nitrate solution. A bright yellow precipitate of barium chromate appears if CrO_4^{2-} is present.



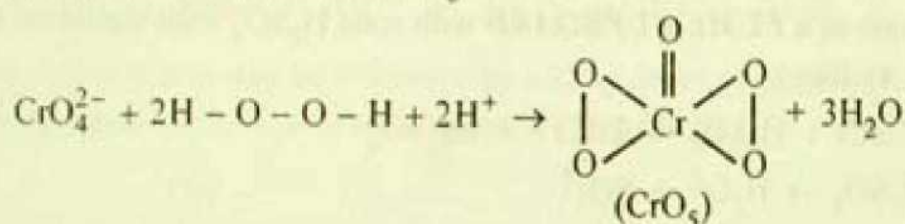
Note: Lead acetate also forms yellow precipitate of lead chromate, but its use is not

recommended as chloride, if present, may form white precipitate of PbCl_2 , which may obscure the yellow colour of PbCrO_4 .

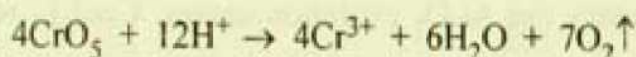
(2) Peroxochromic acid test

(a). Take 1-2 drops of the yellow oxidative fusion extract in a semi-micro test tube, acidify with dil. H_2SO_4 , add 1-2 ml of diethyl ether (or, isoamyl alcohol) and a few drops of hydrogen peroxide (10-volume). A blue colouration is formed, which is extracted into the organic layer on shaking.

In presence of dilute sulfuric acid, CrO_4^{2-} ion reacts with H_2O_2 to form chromim peroxide, $[\text{Cr}(\text{O}_2)_2(\text{O})]$ or chromium pentoxide CrO_5 .



(b). Perform the peroxochromic acid test as above without adding diethyl ether (or isoamyl alcohol). The blue colour appears but fades rapidly with evolution of oxygen, as CrO_5 decomposes in aqueous solution,



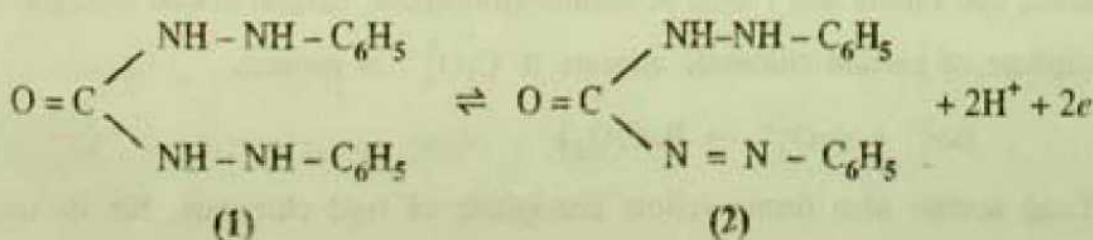
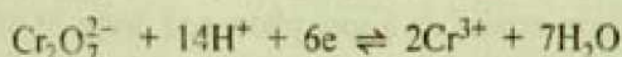
(3) Diphenylcarbazide test

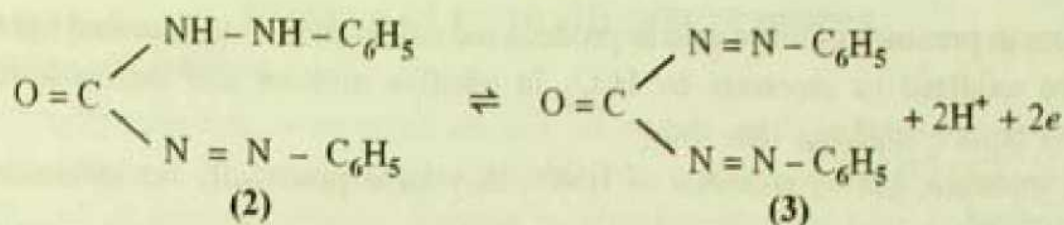
Reagent: 1% solution of diphenylcarbazide in ethanol.

In dilute sulfuric acid medium, diphenylcarbazide (1) reacts with Cr(VI) to produce a soluble intense violet coloured complex, which is very characteristic of Cr and very trace quantity of chromium can be detected from its colour.

When chromate (CrO_4^{2-}) solution is acidified, it is transformed to dichromate, $\text{Cr}_2\text{O}_7^{2-}$ ion. Dichromate in acid medium oxidizes diphenylcarbazide (1) initially to colourless diphenyl carbazone (2) and finally to light yellow diphenylcarbazone (3) and itself is reduced to lower valent chromium.

Both diphenylcarbazide and diphenylcarbazone react with dichromate ion to produce the intense violet colouration. The high intensity of the colour possibly arise from charge transfer transitions.





(a) Place a drop of the yellow oxidative fusion extract on a spot plate, add drops of dil. H_2SO_4 (1 M) until acidic and then drops of the diphenylcarbazide reagent. An intense violet colour appears if chromium is present.

Limit of identification: 0.5γ of Cr

Limit of dilution: 1 : 1×10^5

(b) Alternatively, the preliminary oxidation of Cr(III) salt to chromate may be carried out on the spot plate itself as follows.

Place a drop of the weakly acidic test solution on a spot plate, add 1 drop of saturated bromine water and drops of dil. KOH solution (2 M) until alkaline to litmus. Mix thoroughly. To destroy the excess bromine (if any) add a crystal phenol or sulfosalicylic acid, which consumes the unreacted bromine to form their bromo derivatives [cf. p-304]. Then add 1 drop of diphenylcarbazide reagent and finally drops of dil. H_2SO_4 (1M) until acidic. The red colour of the reaction product between diphenylcarbazide and alkali disappears and an intense violet colouration is produced if chromium is present.

Fe, Cu, Mn, Ni and Co salts interfere in this procedure, as their hydroxides are precipitated by alkali. The test may be applied by removing the precipitates by filtration through cotton filter (cf. Fig. 3.19 a)

Limit of identification: 0.25γ of Cr

Limit of dilution: 1 : 2×10^6

(c) Alternatively, place a drop of the weakly acidic test solution on a spot plate, add 2 drops of (0.1N) potassium peroxodisulfate, $\text{K}_2\text{S}_2\text{O}_8$ (or ammonium peroxodisulfate, $(\text{NH}_4)_2\text{S}_2\text{O}_8$) and 1 drop of silver nitrate solution (0.1 M). Allow to stand for 2-3 minutes and then add 1 drop of the diphenylcarbazide reagent. An intense violet colour is developed if chromium is present.

Mn, if present, is oxidized to purple coloured permanganic acid (HMnO_4). Hg-salts, (vanadate, molybdate)* give blue-violet colour with the reagent in acid medium. If some oxalic acid is added, permanganate is reduced to Mn^{2+} salt, and molybdate is masked by forming oxalatocomplex, $\text{H}_2[\text{MoO}_3(\text{C}_2\text{O}_4)]$.

Limit of identification: 0.8γ of Cr

Limit of dilution : 1 : 6×10^5

4. Test with chromotropic acid reagent

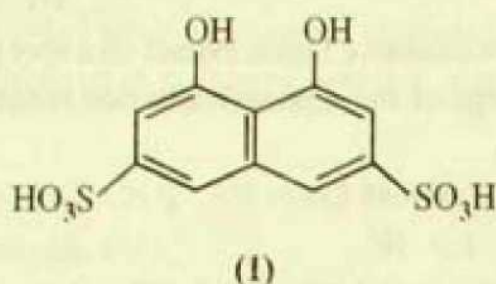
Reagent: Saturated solution of chromotropic acid in water.

Chromotropic acid (i.e., 1,8-dihydroxynaphthalene-3, 6-disulfonic acid, 1) reacts with alkali

*Rare elements

metal chromates in presence of nitric acid to produce red colouration in transmitted light. Cr(III) salts are to be oxidized to chromate by H_2O_2 in alkaline medium and then acidified with dil.HNO_3 (2N) before applying this test.

Fe, U, Ti interfere, but in presence of HNO_3 they have practically no influence.



In 2 N acid medium, chromate (CrO_4^{2-}) is transformed to dichromate ($\text{Cr}_2\text{O}_7^{2-}$), which oxidizes chromotropic acid (I) to a quinoidal compound, which is responsible for the formation of the coloured product, possibly with Cr(III).

Place a drop of the test solution (i.e. the oxidative fusion extract) in a semi-micro test tube, add a drop of 8M HNO_3 and dilute to ~ 2 ml with water and then add 1 drop of the reagent. A red colouration is observed with a white light behind the tube if chromium is present.

Limit of dilution : 1 : 5×10^3

4.14 Reactions of Cobalt (Co^{II} , Co^{III})

Indication

(1) Borax bead test

Blue bead of cobalt metaborate, $\text{Co}(\text{BO}_2)_2$, or the complex salt, $\text{Na}_2[\text{Co}(\text{BO}_2)_4]$, is formed both in oxidizing as well as in reducing flames. Even the presence of large amount of Ni does not interfere.

(2) Intense green colouration

(a) With conc. HCl

Solid sample or weakly acidic or neutral test solution of cobalt (II) salt on boiling with conc. HCl forms intensely green coloured tetrachlorocobaltate (II) complex, CoCl_4^{2-} ion, which on dilution with water, turns purple coloured due to regeneration of the $\text{Co}^{\text{II}}(\text{aq})$ ion, $\text{Co}(\text{H}_2\text{O})_6^{2+}$,



(b) With H_2O_2 - Na_2CO_3 solution

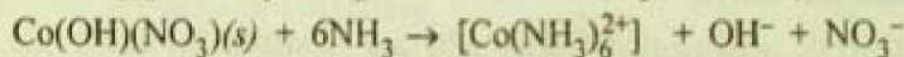
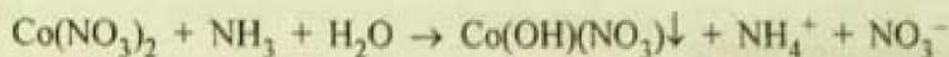
Take a drop of the weakly acidic or neutral test solution on a spot plate or in a semi-micro test tube, add 1 drop of H_2O_2 (10-volume) and 1-2 drops of saturated solution of Na_2CO_3 . A deep green colouration or precipitate appears due to the formation of Co(III) - carbonate complex.



Reactions of cobalt (II) salts in solution

(1) Ammonia solution

When Co(II) salts react with small amount of $aq\text{-NH}_3$ in the absence of ammonium salts, blue coloured basic Co(II) salts are precipitated. The precipitate is soluble in excess of NH_3 , and in solution of ammonium salts, forming brownish yellow solution of hexaammine Co(II) complex:



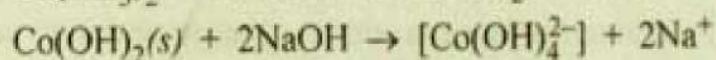
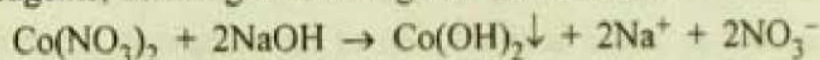
On passing air through the ammoniacal solution of Co(II), or, more rapidly, on addition of H_2O_2 , the brown-yellow colour of complex $[\text{Co(NH}_3)_6]^{2+}$ ion turns red, due to its oxidation to Co(III) ammine complex, $[\text{Co(NH}_3)_6]^{3+}$ (OH)₃:



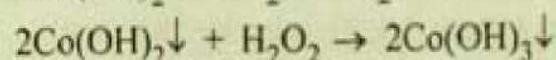
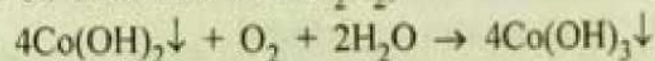
The Co(III) ammine complexes are not affected by alkali hydroxide solutions.

(2) Sodium hydroxide solution

When Co(II) salts are treated with caustic alkali solution, blue coloured basic salts are first precipitated, which upon warming with excess alkali, are converted to pink coloured precipitate of Co(II) - hydroxide. Small amount of the precipitated Co(OH)_2 passes into solution in excess of the reagents, forming a bluish green colouration.



Precipitated Co(OH)_2 , is oxidized to brownish black coloured Co(III) hydroxide on exposure to air or on treatment with H_2O_2 ,



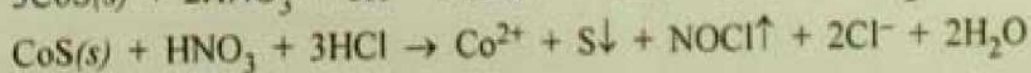
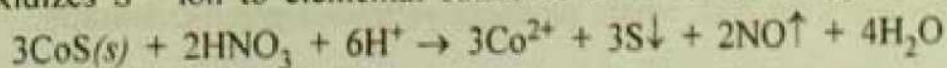
Precipitated Co(OH)_2 is soluble in $aq\text{-NH}_3$ and in concentrated solutions of ammonium salts if the solution is ammoniacal, due to the formation of brownish yellow coloured Co(II) ammine complex, $[\text{Co(NH}_3)_6]^{2+}$ ion (discussed before).

(3) Ammonium sulfide solution

Black precipitate of Co(II) - sulfide is formed on treatment of neutral or ammoniacal solution of Co(II) salts with $(\text{NH}_4)_2\text{S}$ solution:



Although CoS is not precipitated in dil.HCl medium, but the precipitate undergoes so rapid aging that it becomes insoluble in HCl. It dissolves only in hot conc. HNO_3 or in aqua-regia, which oxidizes S^{2-} ion to elemental sulfur or even to sulfate (cf. Sect 4.15).



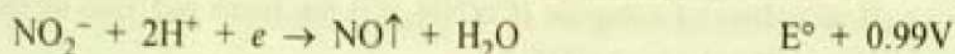
(4) H₂S-water

No precipitate is formed if dil.HCl solution of Co(II) salt is treated with H₂S-water. However, on rendering the solution ammoniacal, black precipitate of CoS appears, but the precipitate does not dissolve in dilute mineral acids (as described above).

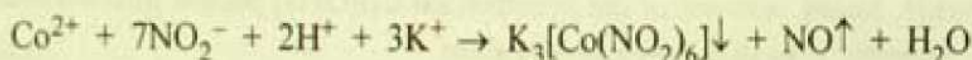
Confirmation

(1) Test with potassium nitrite

In neutral or in dil.acetic acid slution Co(II) salts are oxidized by nitrite ion to yellow coloured cobaltinitrite complex, [Co(NO₂)₆]³⁻, of which the potassium salt being sparingly soluble, a yellow precipitate of potassium cobaltinitrite is formed.



Although $E^\circ(\text{Co}^{3+}/\text{Co}^{2+})$ is much higher than $E^\circ(\text{NO}_2^- + \text{H}^+/\text{NO})$, but the formal potential of $\text{Co}^{3+}/\text{Co}^{2+}$ system becomes much lower due to complex formation of Co^{3+} with NO_2^- ion. Relative stability of the $\text{Co}^{3+} - \text{NO}_2^-$ complex is sufficiently higher than that of the $\text{Co}^{2+} - \text{NO}_2^-$ Complex. Both these factors effect the oxidation of Co^{2+} to Co^{3+} by NO_2^- ion (cf. Sect 2.4). The overall reaction is,



Place 1-2 drops of the neutral or acetic acid solution of the sample in a semi-micro test tube, add drops of freshly prepared saturated potassium nitrite solution and stirr with a glass rod. Warm slightly if necessary and scratch the sides of the test tube with the glass rod. Yellow crystalline precipitate appears if cobalt is present.

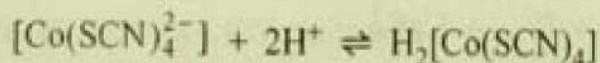
Note: (1) By this test K^+ and NO_2^- ion can also be detected.

(2) Co(II) salts may be differentiated from Ni(II) salts by this test.

(2) Vogel's reaction: Ammonium or Potassium thiocyanate (NH₄SCN or KSCN)

Reagent: Saturated solution of NH₄SCN/KSCN in acetone.

In neutral or weakly acidic solution, Co(II) salts react with NH₄SCN or KSCN to form intensely blue coloured tetrathiocyanatocobaltate(II) complex, [Co(SCN)₄]²⁻ ion.



In presence of conc.HCl, the free complex metallo acid, H₂[Co(SCN)₄], is formed, which is extractable into organic solvents, such as diethylether, iso-amyl alcohol, forming blue-violet organic layer (distinction from Ni^{II}, which produces yellowrsh-green colouration with thiocyanate).

(a) Place 1-2 drops of the slightly acidic test solution in a semi-micro test tube and add a few drops of the thiocyanate solution in acetone. A blue colouration is produced. Add a few drops of diethyl ether or *iso*-amyl alcohol and shake vigorously. The organic layer turns blue-violet if cobalt is present.

Cu(II) salts interfere, by forming red-brown colouration or precipitate of $\text{Cu}(\text{SCN})_2$. Cu(II) may be reduced to Cu(I) by SO_2 -water or sodium sulfite in dil.HCl medium and precipitated as Cu_2I_2 which does not interfere.

Fe(III) forms blood-red coloured $[\text{Fe}(\text{SCN})^{2+}]$ complex and interfere. Fe(III) maybe rendered harmless by masking it in the form of its fluoro complex, $[\text{FeF}_6^{3-}]$ ion, which is colourless or by reducing Fe(III) to Fe (II) with thiosulfate solution. Molybdates* in presence of strong reducing agents, such as Sn(II) chloride, gives red colouration with thiocyanate due to the formation of $\text{H}_3[\text{Mo}(\text{SCN})_6]$ complex. Molybdate may be rendered inactive by adding a drop of phosphoric acid or complexing with oxalic acid or tartaric acid.

(b) Test for Co(II) in presence of Cu(II)

If the colour of the test solution is blue or if Cu is suspected, take 1 ml of the weakly acidic test solution in a centrifuge tube, add a few crystals of Na_2SO_3 and shake. Cu(II), if present, will be reduced to colourless Cu(I). Add drops of KI solution, white precipitate of cuprous iodide, Cu_2I_2 , appears. Brown colour of I_2 will not be visible as the test solution contains sulfite. Centrifuge and treat the centrifugate with the thiocyanate reagent and ether/amyl alcohol as described above.

Limit of identification : 0.5γ of Co.

Limit of dilution: 1 : 1×10^5

(c) Test for Co(II) in presence of Fe(III)

Place 1-2 drops of the weakly acidic test solution on spot plate, add a few crystals of ammonium bifluoride and 5 drops of 10% solution NH_4SCN in acetone. A blue colouration is produced if Co(II) is present.

Limit of identification: 1γ of Co

Limit of dilution: 1 : 5×10^4

(3) Test with sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$)

In neutral solution Co(II) salts react with concentrated solution of sodium thiosulfate to produce blue colouration due to the formation of the complex, $[\text{Co}(\text{S}_2\text{O}_3)_2^{2-}]$ ion. Metal ions forming ammine-complexes, eg, Cu^{2+} , Zn^{2+} , Ni^{2+} , Pd^{2+} do not interfere. Fe(III) salts give transient violet colouration with $\text{S}_2\text{O}_3^{2-}$ ion due to the formation of $[\text{Fe}(\text{S}_2\text{O}_3)_2^-]$, which reacts with unreacted Fe^{3+} ion to form Fe^{2+} and colourless tetrathionate ($\text{S}_4\text{O}_6^{2-}$) ion. The decolourization is accelerated in presence of traces of Cu(II) salts (*cf.* p-259).

*Rare element

Take a few crystals of sodium thiosulfate on a spot plate and add 1 drop of the neutral test solution. A more or less intense blue colouration is produced within a few minutes depending upon the amount of cobalt present. The colour reaction is accelerated if 1 drop of alcohol is added.

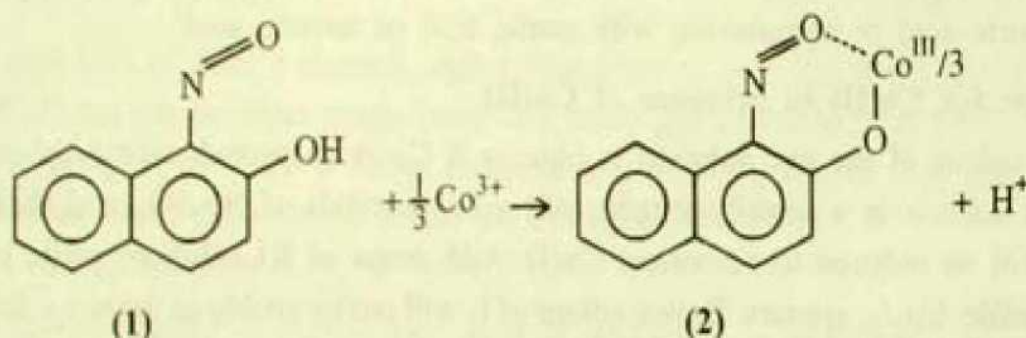
Limit of identification: 8γ of Co

Limit of dilution: 1 : 6250

(4) Test with 1-nitroso-2 naphthol (1N2N)

Reagent: Dissolve 1 g of 1-nitroso-2-naphthol in 50 ml of glacial acetic acid and dilute the solution to 100 ml.

1-Nitroso-2-naphthol (1N2N, 1) reacts with Co(III) in dilute acetic acid medium to form redish-brown crystalline precipitate of the inner metallic Co (III) chelate complex (2).



The precipitate maybe extracted in to chloroform to give a wine-red coloured solution. This is a reaction of Co(III) salt. Although the reagent itself may oxidize Co(II) to Co(III) under the experimental condition, but it is convenient to oxidize Co(II) to Co(III) before applying this test.

Take 1-2 drops of the neutral or weakly acidic test solution in a semi-micro test tube, add 1-2 drops of 10-volume H_2O_2 and 1 drop of NaOH solution (~2M). A black precipitate of Co(III) hydroxide will be formed. Warm on a water bath for ~2 minutes to coagulate the precipitate. Wash the precipitate with water by centrifugation. Dissolve the black precipitate in hot dilute acetic acid and add 1-2 drops of the 1N2N reagent. A red brown crystalline precipitate is formed if cobalt is present.

Limit of identification: 0.05γ of Co.

Limit of dilution: 1 : 1×10^6

Iron (III), copper (II), uranium (IV)*, paladium (II)* also give coloured precipitate with 1N2N. Copper may be transformed into sparingly soluble Cu_2I_2 by treating with KI solution.



Cu_2I_2 may be removed by centrifugation and the brown colour of the centrifugate due to free iodine may be removed by adding sodium sulfite. Co(II) in the resulting solution may be converted to Co(III) and tested with 1N2N as described above.

*Rare elements

Interference due to iron(III), copper (II) and uranium (IV) may be eliminated by precipitating these metal ions as their sparingly soluble phosphates by treating the test solution with sodium or ammonium dihydrogen phosphate in acetic acid-sodium acetate buffer medium (pH-4.5-5), when Co(II) remains in solution, but the interfering metal ions are precipitated as their phosphates, as the solubility products (pK_{sp} values) imply:

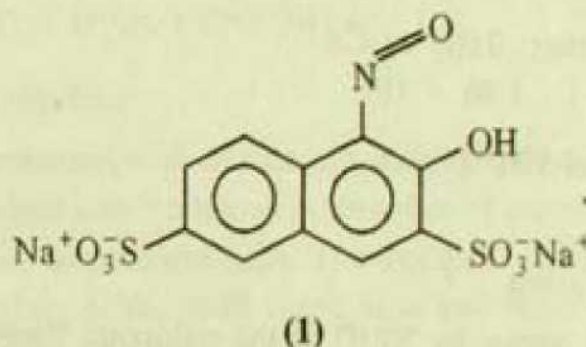
	CoHPO ₄	FePO ₄	U(HPO ₄) ₂	Cu ₃ (PO ₄) ₂
pK_{sp}	6.7	21.9	27.5	36.9

After removing the precipitated phosphates by centrifugation, the Co(II) in the centrifugate may be converted to Co(III) and tested with 1N2N reagent as described above.

(5) Test with nitroso-R-salt reagent

Reagent: 1% solution of nitroso-R-salt in water.

Sodium-1-nitroso-2-hydroxynaphthalene-3, 6-disulfonate, trivially named as nitroso-R-salt (1) is similar to 1-nitroso-2-naphthol (1N2N) reagent in its reactions with metal ions. The only difference is, because of the presence of the sulfonate group, the reagent and its metal complexes are water soluble. Instead of forming coloured precipitate as does 1N2N, nitroso-R-salt forms intensely coloured solutions with metal ions.



For carrying out test for cobalt, the test solution containing Co(II) salt should be oxidized with H₂O₂-NaOH mixture to form black Co(III) hydroxide, and the latter after decomposition of excess H₂O₂ should be dissolved in acetic acid as described under test with 1N2N reagent. The resulting test solution, containing Co(III), should be subjected to test with the reagent.

Take 1-2 drops of the oxidized test solution in a semi-micro test tube, add 1-2 drops of sodium acetate solution (saturated) and then 2-3 drops of the reagent. A red colouration is produced if cobalt is present.

The test is applicable in presence of nickel. Iron and tin interfere and should be removed. Iron (III) can be masked as [FeF₆³⁻] complex by adding 1-2 crystals of NH₄F or KF or NaF. Tin, if present, should be removed as sulfide with H₂S - water in HCl medium.

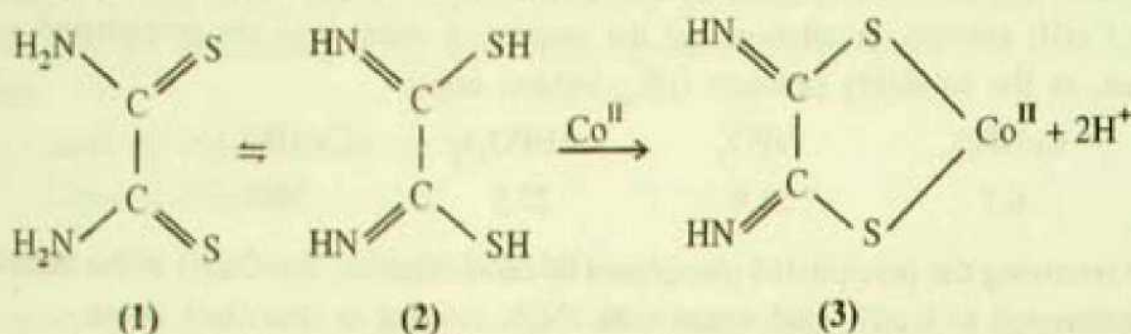
Limit of dilution: 1 : 5 × 10⁶

(6) Test with rubeanic acid reagent

Reagent: 1% solution of rubeanic acid in ethanol.

In presence of ammonium or sodium acetate, Co(II) salts react with alcoholic solution of

rubeanic acid (1) forming a yellow-brown precipitate of Co(II) rubeanate complex (3) with the dithiol (or diimido) form (2) of the reagent.



Although the precipitate of Co(II)-rubeanate (3) is formed in basic solution, but once formed, the precipitate does not dissolve in mineral acids.

Ni(II) and Cu(II) salts react with rubeanic acid under the same experimental condition, producing respectively blue and black precipitates. Large excess of ammonium salts reduce the sensitivity of the test.

Place a drop of the test solution on a drop reaction paper and hold the same over ammonia and then add a drop of the rubeanic acid reagent. A yellow-brown fleck or a ring is formed if cobalt is present.

Limit of identification: 0.03γ of Co

Limit of dilution: 1 : 1.66×10^6

4.15. Reactions of Nickel (Ni^{II})

Indication

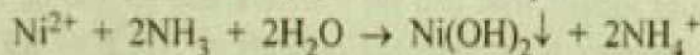
(1) Borax bead colouration

Borax bead is coloured brown by Ni(II) in the oxidizing flame due to the formation of Ni(II)-metaborate, Ni(BO₂)₂, or, complex metaborate, Na₂[Ni(BO₂)₄] and grey in the reducing flame due to the formation of metallic nickel.

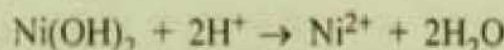
Reactions of Ni(II) ions in solution

(1) Ammonia solution

When Ni(II) salt solutions are treated with aq-NH₃ solution, green precipitate of Ni(OH)₂ is first formed. The precipitate dissolves in excess ammonia producing deep blue colouration due to the formation of Ni(II) ammine complexes:



The precipitate is also soluble in dilute acids,



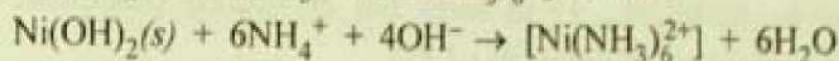
If ammonia is added in presence of ammonium salts, the precipitate of Ni(OH)₂ is not formed, but blue colouration due to the ammine complex, [Ni(NH₃)₆]²⁺ ion, is formed immediately.

(2) Sodium hydroxide solution

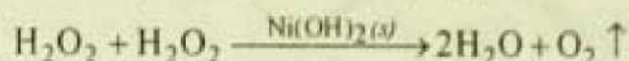
When Ni(II) salt solutions are treated with NaOH solution, green precipitate of Ni(OH)₂ appears. The precipitate is insoluble in excess NaOH solution (distinction from chromium).



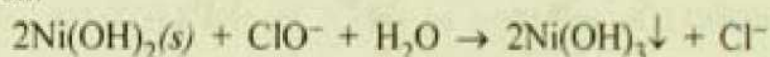
The precipitate is soluble in ammonia solution and also in solution of ammonium salts in presence of caustic alkali, producing deep blue colouration due to the formation of hexaammine nickel (II) complex, [Ni(NH₃)₆]²⁺ ion.



The deep blue colour of complex [Ni(NH₃)₆]²⁺ ion may be mistaken with the intense blue colour of [Cu(NH₃)₄]²⁺ ion. [Ni(NH₃)₆]²⁺ complex, is not oxidized on exposure to air or on treating with H₂O₂ to higher valent nickel complexes (distinction from cobalt). Ni(II)-hydroxide, on the other hand, catalyses the disproportionation of H₂O₂.



Precipitated Ni(OH)₂, may however, be oxidized to Ni(III) hydroxide by hypochlorite (OCl⁻) ion:

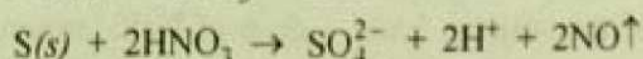
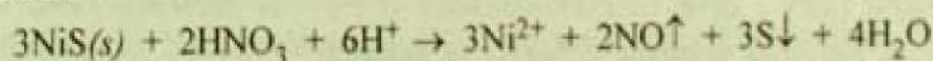


(3) Ammonium sulfide solution

Ni(II) salt solutions, on treatment with ammonium sulfide reagent produce black precipitate of Ni(II)-sulfide, NiS, which becomes colloidal in presence of excess of the reagent and also in presence of large excess of ammonium salts. The colloidal solution may be coagulated by boiling, or, rendering slightly acidic with acetic acid and boiling.



Although not precipitated in dilute HCl medium, NiS, like CoS, once precipitated, does not dissolve in dilute HCl (distinction from MnS and ZnS) and also in acetic acid. Possibly the precipitate undergoes rapid aging and transforms into a more compact structure, which is not attacked by dilute acids. The precipitate dissolves in hot conc. HNO₃ and also in aqua-regia with separation of sulfur, which on prolong digestion, is oxidized to sulfate ion and passes into solution:



(4) H₂S -water

When Ni(II) salts in neutral solution, are treated with H₂S - water, NiS is only partly

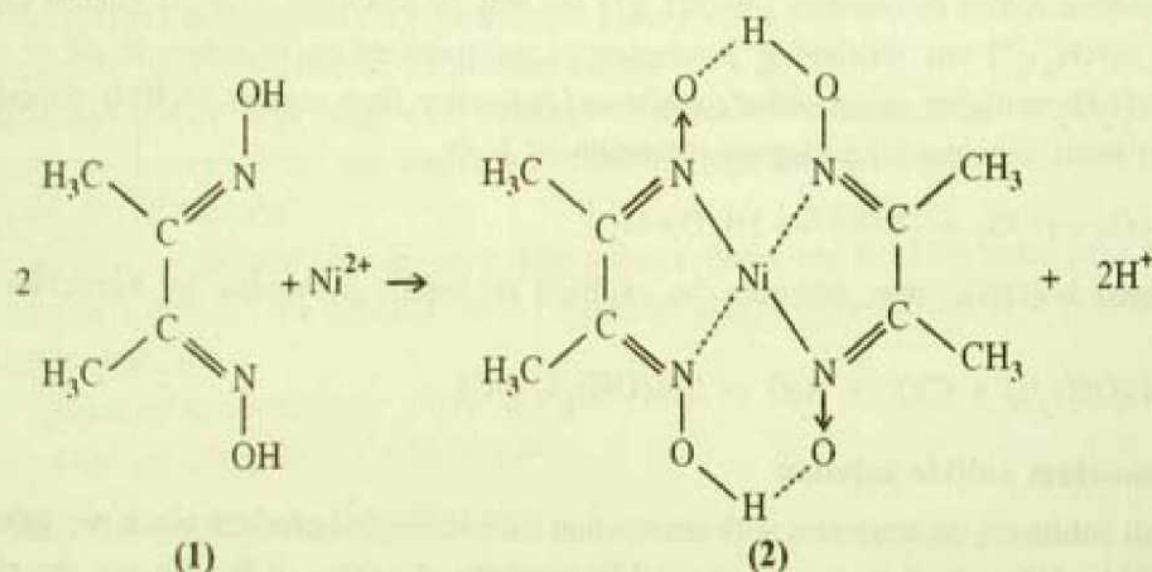
precipitated, but no precipitation occurs in solutions containing mineral acids. However, complete precipitation of NiS occurs from ammoniacal or alkaline solution (*cf.* reactions with $(\text{NH}_4)_2\text{S}$ solution).

Confirmation

(1) Test with dimethylglyoxime (DMGH_2) reagent

Reagent: 1% solution of dimethylglyoxime in alcohol.

In faintly ammoniacal solution, or, in solution made just alkaline with sodium acetate, Ni(II) salts react with dimethylglyoxime (DMGH_2 , 1) to form red crystalline precipitate of bis-dimethylglyoximate nickel (II) complex, $[\text{Ni}(\text{DMGH})_2]$ (2).



Cu^{2+} in ammoniacal medium gives violet colored soluble complex with DMGH_2 . Fe^{2+} (gives red colouration), Co^{2+} (produces brown colouration), Bi^{3+} (forms yellow precipitate) interfere in ammoniacal solution. Fe^{3+} is precipitated as $\text{Fe}(\text{OH})_3$ in ammoniacal medium and obscure the test. Palladium and platinum give precipitate even in acidic solution. Gold salts are reduced to metallic gold. Most metal ions that form hydroxide precipitate with *aq.* NH_3 interfere. Fe^{3+} ion may be masked with NaK-tartrate. Interference due to Fe^{2+} may be eliminated by oxidizing it with H_2O_2 in ammoniacal medium, then masking the resulting Fe^{3+} with NaK-tartrate solution.

(a) Place a drop of the neutral or weakly acidic test solution on a drop-reaction paper, add a drop of the reagent (and 1 drop of NaK-tartrate if Fe^{3+} is present). Hold the paper over ammonia vapour. A red spot appears if Ni(II) is present.

(b) Alternatively, take 1-2 drops of the weakly acidic or neutral test solution in a semi-micro test tube or on a spot plate, add 1 drop of the reagent. [Add 1 drop of NaK-tartrate if Fe^{3+} is present]. Then add drops of dilute ammonia solution. A red crystalline precipitate is formed if Ni(II) is present. A red colouration may be produced if small amount of Ni(II) is present.

Limit of identification: 0.16γ of Ni, 0.5γ of Ni in presence of Fe

Limit of dilution: 1 : 3×10^6 , 1 : 1×10^5 in presence of Fe.

(c) Test of Ni(II) in presence of Cu(II), Co(II) and Mn(II)

Place a drop of the weakly acidic test solution on a spot plate, add 1 drop of H_2O_2 (10-volume) and 1 drop of Na_2CO_3 solution (saturated). If Co(II) is present it is oxidized to Co(III), forming a green solution, which gradually darkens and black precipitate of Co(III) oxide appears. Mn(II), if present, is oxidized and precipitated as black MnO_2 . Cu(II) is also precipitated first as basic salt then as black $\text{Cu}(\text{OH})_2$. Add 1 drop of alcoholic DMGH_2 solution. Red precipitate of $\text{Ni}(\text{DMGH})_2$ is formed and slowly rises to the surface of the liquid, because of lower surface tension of alcohol.

Limit of identification: 1.25γ of Ni (in presence of 200 times of Co)

Limit of dilution: 1 : 4×10^4

(d) Test of Ni(II) with paper impregnated with DMGH_2 reagent

Soak a strip of Whatman No. 1 filter paper in alcoholic solution of DMGH_2 and allow the paper to dry. Place a drop of the weakly acidic or neutral test solution on the reagent paper and allow it to dry. Immerse the paper in a bath of dilute ammonia solution and keep it in gentle motion. Coloured dimethylglyoximate compounds of copper and cobalt are dissolved and red fleck of $\text{Ni}(\text{DMGH})_2$ remains on the white background of the paper.

(e) DMGH_2 test of Ni(II) in presence of oxidizing agents

In presence of large excess of oxidizing agents, the red precipitate of $\text{Ni}(\text{DMGH})_2$ is not formed, a red to orange colouration is formed instead. Red $\text{Ni}(\text{DMGH})_2$ on treatment with suitable oxidant in alkaline medium is transformed into a pink solution, which possibly consists of Ni(IV) and/or an oxidation product of DMGH^- ion.

Place a drop of the test solution on a spot plate, add 1-2 drops of saturated bromine water (or, a small crystal of $\text{K}_2\text{S}_2\text{O}_8$ or $(\text{NH}_4)_2\text{S}_2\text{O}_8$) and a drop of 0.1 M AgNO_3 solution. After 2-3 minutes, render the solution ammoniacal. Bromine colour disappears. Add a few more drops of ammonia solution. A red to orange colour remains if nickel is present.

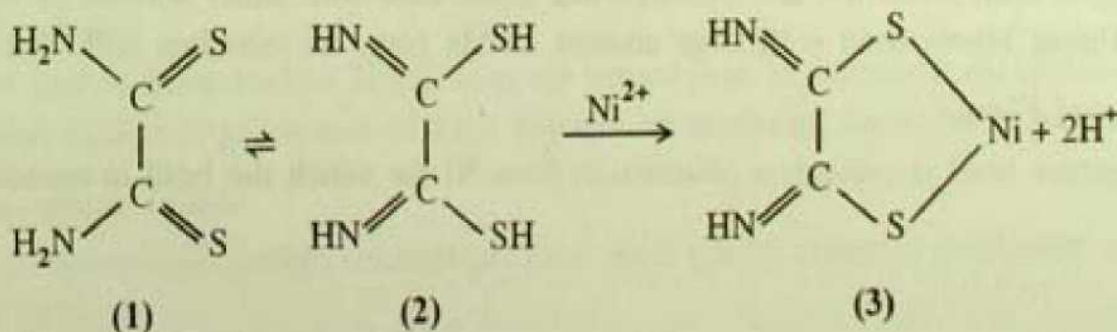
Limit of identification: 0.12γ of Ni

Limit of dilution: 1 : 4×10^5

(2) Test with rubeanic acid

Reagent: 1% alcoholic solution of rubeanic acid.

Ni(II) salts in ammoniacal medium, react with rubeanic acid (1) to form blue to blue-violet precipitate of Ni(II)-rubeanate (3) with the dithiol (or diimide) form (2) of the reagent.



Cu(II) gives a black precipitate and Co(II) gives a brown precipitate with the reagent and interfere. Cu(II), Co(II) and Ni(II) rubeanates, although are precipitated in ammoniacal medium, but are not soluble in dilute mineral acids. Possibly the precipitated complexes undergo rapid aging, leading to polymeric materials. [Cf. reaction with Cu(II), p. 260].

(a) Place a drop of the test solution on a drop reaction paper and hold it over ammonia vapor for 1-2 minutes. Add a drop of the alcoholic solution of rubeanic acid. A blue to blue-violet stain is formed depending upon the quantity of Ni(II) present.

Limit of identification: 0.012% of Ni (in 0.015 ml)

Limit of dilution: 1 : 1.25×10^6

(b) Rubeanic acid test of Ni(II) in presence of Fe(III), Cu(II) and Co(II) by capillary separation of ammine complexes

Taking advantage of the fact that the ammine complexes, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Co}(\text{NH}_3)_6]^{2+}$ and $[\text{Ni}(\text{NH}_3)_6]^{2+}$ differ in their diffusion velocities on filter paper, it is possible to create capillary separation of these ammine complexes and to detect Ni^{II} , Cu^{II} and Co^{II} from the colours of their rubeanate complexes.

Place a drop of an ammoniacal test solution containing Co(II), Ni(II) and Cu(II) in mixture on a drop reaction paper and hold the paper over ammonia vapour for some time. If Ni(II) is present, the complex $[\text{Ni}(\text{NH}_3)_6]^{2+}$ ion moves fastest and so it accumulates in the outer zone of the spot. Add a drop of the alcoholic solution of rubeanic acid at the periphery of the paper. As the reagent drop coalesces with the outer zone of the test solution, a blue ring of Ni(II) rubeanate is formed encircling the brown to green or brown circle due to Cu(II) and Co(II) rubeanates.

This test of Ni(II) can also be carried out in presence of Fe(III), which is precipitated as brown $\text{Fe}(\text{OH})_3$ in ammoniacal solution, while the $[\text{Ni}(\text{NH}_3)_6]^{2+}$ complex ion diffuses out and reacts with the reagent applied from the side of the paper, forming a blue ring around the brown spot of $\text{Fe}(\text{OH})_3$.

4.16 Reactions of Manganese (Mn^{II} , Mn^{III} , Mn^{IV} , Mn^{VI} , Mn^{VII})

Indication

(1) Borax bead colouration

Oxidizing Flame:

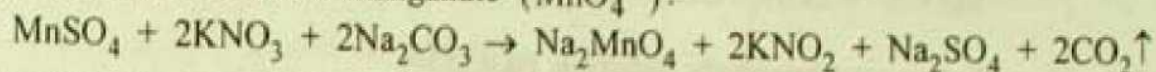
- (i) Violet bead when hot and amethyst-red when cold with small amount of Mn.
- (ii) Almost brown bead with large amount of Mn (may be mistaken with that of Ni).

Reducing Flame:

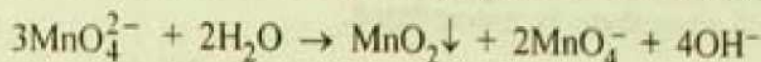
Manganese bead is colourless (distinction from Ni for which the bead in reducing flame is grey).

(2) Oxidative fusion test

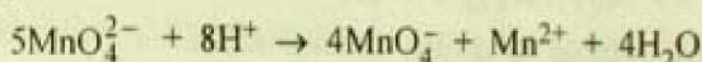
When manganese salts are fused with sodium carbonate in presence of an oxidizing agent, such as, potassium nitrate on a mica foil or on a platinum wire loop, a green mass is produced due to the formation of alkali manganate (MnO_4^{2-}).



The green mass on extraction with water produces a green solution, which on neutralization with dilute acid (not HCl) produces pink coloured permanganate (MnO_4^-) ion and precipitates MnO_2 in neutral medium through disproportionation reaction (cf. p. 190).



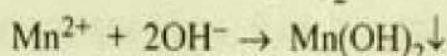
In acidic medium (not HCl), MnO_4^{2-} ion disproportionates to permanganate MnO_4^- and Mn^{2+} ion,



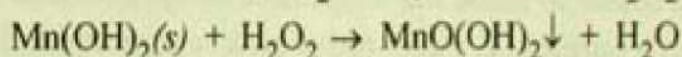
Reactions of Mn(II) salts in solution

(1) Sodium hydroxide solution

On adding dil. NaOH (~2M) solution to Mn(II) salt solution, initially a white precipitate of Mn(II)-hydroxide is formed. The precipitate is insoluble in excess alkali but soluble in dil. HCl. The precipitate slowly becomes brown on exposure to air due to oxidation to black hydrated manganese dioxide, $\text{MnO}(\text{OH})_2$.

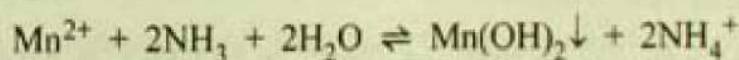


Transformation to black $\text{MnO}(\text{OH})_2$ is rapid if some H_2O_2 is added,



(2) Ammonia solution

White $\text{Mn}(\text{OH})_2$ is partly precipitated when Mn(II) salts are treated with aq- NH_3 solution. The precipitate dissolves on addition of ammonium salts, as due to common ion effect of NH_4^+ ion, the equilibrium,



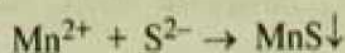
shifts to the left.

(3) H_2S - water

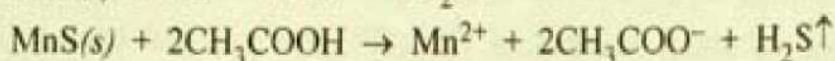
No precipitate is formed when Mn(II) salts are treated with H_2S -water in dil. HCl medium, but pink (flesh coloured) precipitate of MnS appears on rendering the solution ammoniacal.

(4) Ammonium sulfide

Colourless ammonium sulfide solution produces pink (flesh) coloured precipitate of MnS with Mn(II) salts.

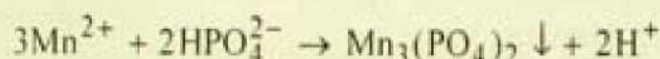
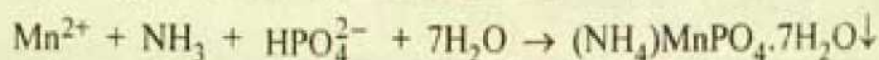


The precipitate is soluble in dil.HCl (distinction from CoS and NiS). The precipitate is even soluble in acetic acid (distinction from CoS, NiS and ZnS).



(5) Disodium hydrogenphosphate solution (0.033M)

In presence of ammonia or ammonium salts, Mn^{2+} reacts with HPO_4^{2-} ion to produce pink precipitate of ammonium manganese phosphate, $\text{NH}_4\text{MnPO}_4 \cdot 7\text{H}_2\text{O}$. In absence of ammonia, or, ammonium salts, binary Mn(II) phosphate is precipitated,



Both the phosphate precipitates are soluble in dilute mineral acids.

Confirmation

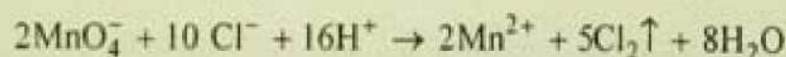
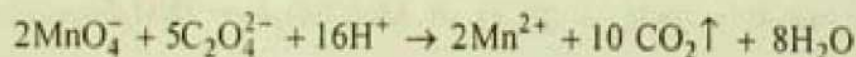
(1) PbO_2 (or Pb_3O_4) – conc. HNO_3 oxidation

Colourless manganese (II) salts are oxidized to pink coloured permanganic acid (HMnO_4) when digested with lead dioxide (PbO_2) or red lead (Pb_3O_4 which is $2\text{PbO} \cdot \text{PbO}_2$) and conc. HNO_3 ,



(a) Place 1 ml of the test solution (not containing HCl or any chloride), or, ~0.1 g of the solid sample in a semi-micro test tube, add small amount of lead dioxide (or red lead) and a few drops of conc. HNO_3 . Boil for 2-3 minutes inside a **FUME CUPBOARD**, dilute with 1-2 ml of water, mix well and allow to settle the suspended solids containing unreacted PbO_2 . The supernatant liquid assumes a purple (i.e, violet-red or pink) colouration, due to the formation of permanganate (MnO_4^-) ion.

(a)(i) Place 2 drops of the purple coloured supernatant liquid obtained in test 1(a), on two adjacent cavities of a spot plate. Add 1-2 drops of HCl in one cavity and 1-2 crystals of oxalic acid in another cavity. Purple colour of MnO_4^- is discharged in both the cavities due to reduction of MnO_4^- ion to colourless Mn^{2+} ion:



(2) Peroxodisulfate oxidation

Mn(II) salts are oxidized to permanganic acid (HMnO_4) by potassium or ammonium peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$ or $(\text{NH}_4)_2\text{S}_2\text{O}_8$) in 2-3 N HNO_3 or H_2SO_4 medium in presence of small amount of Ag^+ which acts as a catalyst.



The Mn(II) solution should be dilute (<0.02M), otherwise MnO_2 may be precipitated.

Chloride, bromide, iodide should be absent. If halides are present, the solid sample should be digested with a few drops of conc. H_2SO_4 to remove the halides. Other reducing agents, if present, may reduce MnO_4^- to Mn^{2+} , which in turn is oxidized back to MnO_4^- by $\text{S}_2\text{O}_8^{2-}$. So the oxidant, $\text{S}_2\text{O}_8^{2-}$ should be added in little excess.

Place a drop of the test solution (or a small amount, <0.1 g of the solid sample) in a micro crucible or in a semi-micro test tube, add ~1 ml of 2-3 N HNO_3 or H_2SO_4 and a drop of 0.1M silver nitrate solution. Heat the mixture to boiling and add a few mg. of solid $\text{K}_2\text{S}_2\text{O}_8$ [or, $(\text{NH}_4)_2\text{S}_2\text{O}_8$] to the hot solution. A purple colour due to HMnO_4 appears immediately if manganese is present.

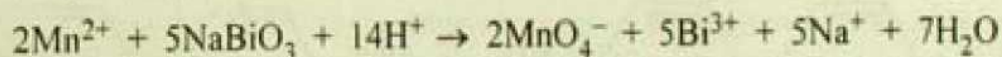
Simultaneous detection of Mn and Cr

If chromium (III) salts, are present, these are oxidized to orange coloured dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ion, which of course does not interfere as its orange colour is often masked by the purple colour of permanganate.

Add a few crystals of oxalic acid to the purple coloured solution obtained after peroxo disulfate oxidation. The purple colour of MnO_4^- ion is discharged. If chromium is also present, an orange colour persists in the solution.

(3) Sodium bismuthate (NaBiO_3) oxidation

Mn (II) salts are oxidized by sodium bismuthate (NaBiO_3) in dilute (2-3 N) HNO_3 or H_2SO_4 medium to purple coloured permanganic acid at ordinary temperature. Cr(III) salts, if present, are also oxidized to orange coloured dichromate ($\text{Cr}_2\text{O}_7^{2-}$), but the reaction is slow at ordinary temperature. Rate of Cr(III) oxidation may be further lowered by carrying out the oxidation at lower temperature ($\sim 15^\circ\text{C}$).



Place 1 drop of the test solution on a spot plate, add 1 drop of conc. HNO_3 and then a small amount of sodium bismuthate. Stir the mixture with a glass rod for 1-2 minutes. The purple colour of permanganic acid appears if manganese is present.

If the solution is intensely dark coloured, dilute the mixture with sufficient water, so that the purple colour is recognisable.

Note: Permanganate may be tested from decolourization of its pink colour by (i) oxalic acid, (ii) Mohr's salt (iii) H_2O_2 , (iv) HCl .

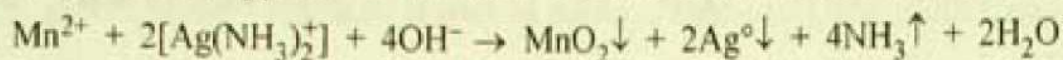
Limit of identification : 0.1γ of Mn

Limit of dilution: 1 : 5×10^5

(4) Test with silver-amine salt

Reagent: To 1 ml of a saturated solution of silver nitrate add drops of conc. NH_3 until the precipitate that is initially formed, passes into solution.

Mn (II) salts are oxidized to black manganese dioxide by ammonical silver nitrate solution. Silver ammine complex, $\text{Ag}(\text{NH}_3)_2^+$ ion, is reduced to finely powdered black metallic silver. This test may also be applied for detection of silver and ammonium salts (*cf.* p.238, 343).



The test may be applied in presence of Al (III), Cr (III), Fe(III), Co(II), Ni (II), Zn (II), Hg(II), Pb(II) and Bi (III) salts. Sensitivity of the test is, however, low if the metal ions which form sparingly soluble coloured hydroxides in ammonical medium are present.

Place 1 drop of the ammoniacal silver nitrate solution on a drop-reaction paper and allow the spot to dry. Add 1 drop of the test solution on the reagent spot. A black spot is formed if Mn(II) salt is present.

Always run a blank test, since ammoniacal silver nitrate solution is slightly reduced to black metallic silver by the filter paper used for the test.

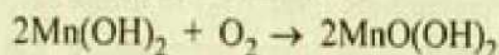
Limit of identification: 0.05γ of Mn

Limit of dilution: 1 : 1 × 10⁶

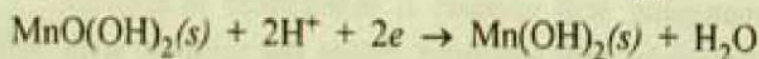
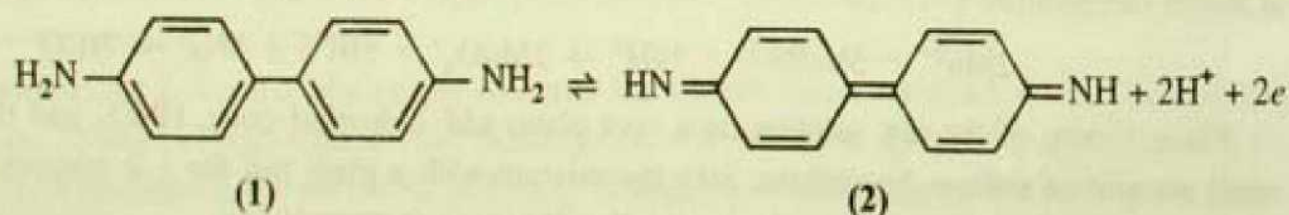
(5) Benzidine blue test

Reagent: Dissolve 0.05 g of benzidine in 10 ml of glacial acetic acid, dilute to 100 ml and filter if necessary. Use the clear filtrate for the tests.

If precipitated manganous hydroxide is exposed to air, it is readily oxidized to hydrated manganese dioxide by oxygen of the air:



Hydrated manganese dioxide oxidizes benzidine (1) to benzidine blue, which is an association compound of benzidine (1) and its oxidation product (2) along with 2 equivalents of a monoprotic acid (*cf.* Sect 4.4).



Place 1 drop of the test solution on a drop reaction paper, add 1 drop of dil. NaOH solution (0.05 N) and 1 drop of benzidine reagent. Add a crystal of sodium acetate if necessary. Blue spot results at places where manganese dioxide is formed. The intensity of the blue colour depends upon the manganese content. The blue colour disappears on drying the paper, but reappears on addition of the benzidine reagent.

Other substances that can oxidize benzidine to benzidine blue, are CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, $[\text{Fe}(\text{CN})_6]^{3-}$, Co(III), Ag(I), [Ti(III), Ce(III & IV)].* Fe(III) may be rendered harmless by complexing it with Na-K tartarate. Ce(III, IV) maybe removed by boiling the test solution for

*Rare elements

some time with calcium fluoride (CaF_2), when cerium fluoride is precipitated on the unchanged CaF_2 . Benzidine blue test maybe applied on the clear solution obtained after centrifugation. Copper may be separated as CuSCN , which may be removed by centrifugation. Ag(I) , Tl(I)^* maybe separated as their chlorides. Chromate may be removed as barium chromate.

Limit of identification : 0.15γ of Mn

Limit of dilution : 1 : 3.3×10^5

(6) Catalytic oxidation to permanganate in alkaline medium

When Mn(II) salts are oxidized to MnO_2 by hypobromite (OBr^-) ion in alkaline medium according to,



if traces of a copper (II) salt is present, Cu(II) is oxidized by BrO^- ion to Cu(III) , which catalyzes the oxidation of Mn^{2+} to MnO_4^- by alkaline hypobromite.



With alkaline hypobromite, Cr(III) salts are oxidized to CrO_4^{2-} . Other metal ions which from insoluble hydroxides do not interfere.

If Ni(II) and Co(II) are suspected, the amount of Cu(II) to be added to the test solution should be excess over the quantity of Ni or Co, before treating with hypobromite.

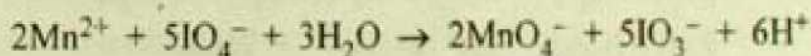
Take 3-4 drops of 1% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution in a test tube, add 1 drop of the test solution and 8-10 drops of 0.1 N sodium hypobromite solution. Boil the mixture for a few minutes. The supernatant liquid becomes red-violet if manganese is present.

Limit of identification : 2.5γ of Mn

Limit of dilution : 1 : 2.5×10^4

(7) Test with periodate and tetrabase: Catalytic reaction of manganese

Mn(II) salts are oxidized to permanganate by sodium or potassium periodate in acetic acid medium:



Large quantities of Mn can be detected from the purple colour of permanganate. For the detection of trace quantities of Mn, small amount of tetrabase (tetramethyl-*p*-diaminodiphenyl methane, *tetrabase*) maybe added, which is oxidized by permanganate to an intense blue oxidation product, that enables the detection of smaller quantities of Mn. MnO_4^- is reduced by tetrabase to Mn^{2+} salt, which is reoxidized to MnO_4^- by IO_4^- ion, This makes the reaction catalytic. Chromium salts interfere in this test and should be absent. Cr(III) salts are oxidized by periodate to Cr(VI) state, which also oxidizes tetrabase to a blue coloured product.

Limit of identification: 0.001γ of Mn

Limit of dilution: 1 : 5×10^7

*Rare element

4.17 Reactions of Zinc (Zn^{II})

Indication

(1) Dry test tube heating

When solid Zn(II) salts are heated in a dry test tube, the salts decompose to form zinc oxide, which is yellow when hot but white when cold. Zinc oxide undergoes crystal defect* when heated and its normal structure is restored when cooled.

(2) Rinmanns green test

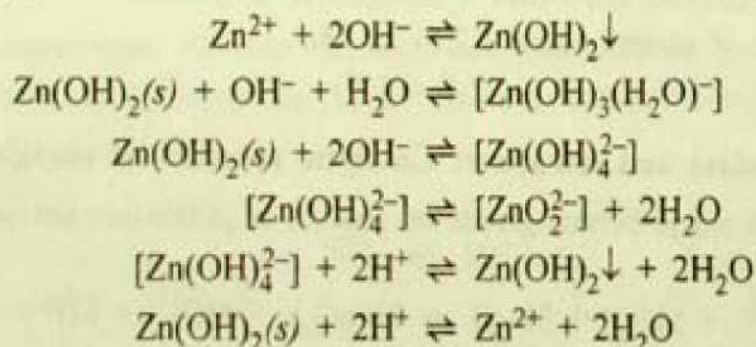
Zinc compounds when heated with cobalt nitrate in presence of charcoal, a green residue of mixed oxide, CoZnO₂ ($\equiv$ CoO.ZnO) is formed, which is green in colour and is known as *Rinmann's green*.

Soak a piece of ashless filter paper (Whatman No. 41) in a Zn(II) salt solution, add 1 drop of cobalt nitrate and ignite the paper in a porcelain or a silica crucible or in a platinum wire coil. A green residue is formed if Zn is present.

Reactions of Zn²⁺ ion in solution

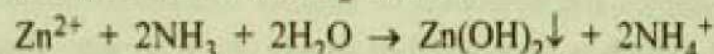
(1) Sodium hydroxide solution (~2M)

Take 1 ml of weakly acidic or neutral test solution and add drops of NaOH solution (~2M). A white precipitate of zinc hydroxide first appears, which dissolves in excess of alkali, producing zincate, Zn(OH)₄⁻ or (ZnO₂)²⁻ ion, due to amphoteric nature of zinc hydroxide. The precipitate of Zn(OH)₂ reappears on acidification and redissolves on addition of excess acid.



(2) Aqueous-ammonia solution

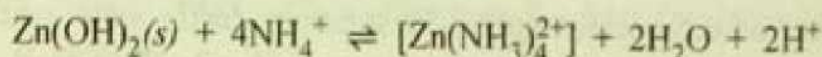
To 1-2 drops of the weakly acidic to a neutral test solution add 1 drop of (1:1) aq-NH₃ solution. A white precipitate of Zn(OH)₂ appears.



The precipitate is not formed if ammonium salts are present. The precipitate dissolves on

* ZnO loses O₂ reversibly at high temperature leaving the electrons of the oxide ions (O²⁻) in the interstices (metal excess *Frenkel defect*): $\text{ZnO} \rightleftharpoons \text{Zn}^{2+} + \frac{1}{2}\text{O}_2 + 2e$. Excitation of these interstitial electrons to higher energy levels may occur on absorption of radiation in the visible region, as a result, ZnO appears yellow when hot. On cooling, the oxygen atom returns to its site and the material again becomes white.

addition of ammonium salts, or excess ammonia, due to the formation of tetraammine zincate (II) complex ion.

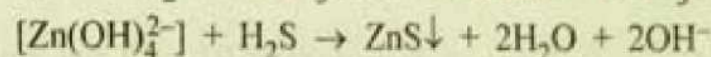
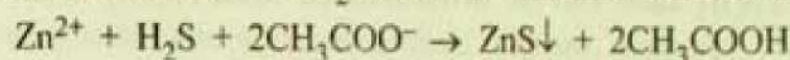


(3) H₂S-water

When acidic (>0.5M) solution of Zn(II) is treated with H₂S-water, no observable change takes place. But treatment of neutral or weakly acidic (pH~3) solution of Zn(II) with H₂S-water gives white precipitate of zinc sulfide:



ZnS is also precipitated when Zn²⁺ is treated with H₂S-water in presence of sodium or ammonium acetate or on addition of H₂S-water to alkaline solution of zincate ion:



Precipitated ZnS is soluble in dil.HCl but insoluble in acetic acid and in dilute alkali.

(4) Ammonium sulfide solution

When weakly acidic or neutral solution of Zn(II) salt is treated with colourless ammonium sulfide solution, white precipitate of zinc sulfide appears. The precipitate is colloidal in nature, but coagulates on boiling with ammonium salts.



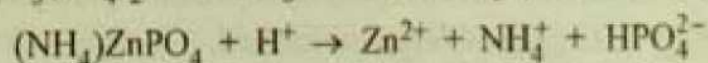
The precipitate is soluble in dil.HCl, but insoluble in acetic acid, ammonia and ammonium salt solutions.

(5) Disodium hydrogenphosphate solution (0.033M)

Treatment of Zn(II) salt solution with disodium hydrogenphosphate in presence of ammonium salts, produces white crystalline precipitate of ammonium zinc phosphate, whereas, in absence of ammonium salts, simple binary phosphate is precipitated:

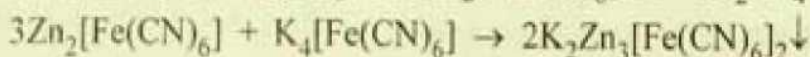
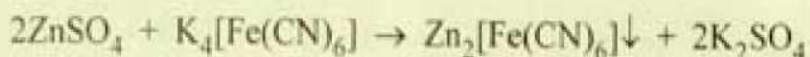


Both the phosphate precipitates are white in colour and are soluble in dilute mineral acids. In concentrated ammonia, both the phosphate precipitates dissolve due to the formation of [Zn(NH₃)₄]²⁺ complex ions:

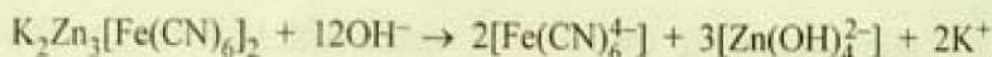


(6) Potassium ferrocyanide $K_4[Fe(CN)_6]$ solution (0.033M)

In neutral or weakly acidic ($pH \sim 5$) solution $Zn(II)$ salts react with potassium ferrocyanide to form white precipitate of zinc ferrocyanide, $Zn_2[Fe(CN)_6]$, which reacts with the excess reagent to form much less soluble double ferrocyanide, potassium zinc ferrocyanide, $K_2Zn_3[Fe(CN)_6]_2$.



The precipitate of potassium zinc ferrocyanide is insoluble in dilute acids, but readily soluble in caustic alkali:



By this reaction, $Zn(II)$ salts can be differentiated from $Al(III)$ salts.

Confirmation

It is convenient to perform confirmatory tests for $Zn(II)$ with the zincate solution after acidification with acetic acid.

Take a small amount (<0.1 g) of the solid sample in a semi-micro test tube, add 1-2 ml of sodium hydroxide solution (~ 2 M) and boil gently for 2-3 minutes. If $Zn(II)$ is present, it passes into the alkali solution in the form of zincate ion ($[Zn(OH)_4]^{2-}$ or ZnO_2^{2-}). If phosphate is present, add 1-2 drops of barium chloride solution until precipitation is complete and then add 1-2 drops of saturated sodium sulfate solution to precipitate unreacted Ba^{2+} ion as $BaSO_4$. Centrifuge and discard the residue. Acidify the centrifugate (which contain zincate ion) with acetic acid and perform tests for $Zn(II)$ with this *prepared solution*. If phosphate is not present, simply acidify the NaOH extract with acetic acid and proceed with this solution.

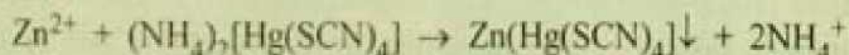
(1) Ammonium mercuriothiocyanate-Copper sulfate reagent

Reagent:

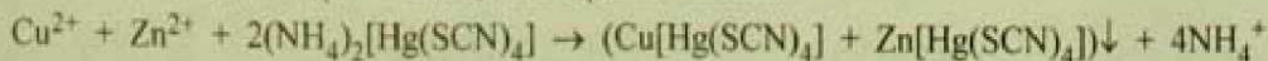
(i) $(NH_4)_2[Hg(SCN)_4]$ ($\sim 0.3M$): Dissolve 9 g. of NH_4SCN and 8 g. of $HgCl_2$ in water and dilute to 100 ml. Allow to stand for 2-3 days, use the clear supernatant liquid.

(ii) $CuSO_4 \cdot 5H_2O$: ($\sim 0.02M$) : 0.5% solution in water.

In dilute acetic acid medium, Zn^{2+} ion alone reacts with ammonium mercuriothiocyanate, $(NH_4)_2[Hg(SCN)_4]$, to form white precipitate of $Zn(II)$ mercuriothiocyanate:



$Cu(II)$ salts alone do not form any precipitate with ammonium mercuriothiocyanate. But if traces of a $Cu(II)$ salt is present along with $Zn(II)$, and the mixture is treated with ammonium mercuriothiocyanate solution, $Cu(II)$ - mercuriothiocyanate coprecipitates with $Zn(II)$ - mercuriothiocyanate, and a violet (or, blackish purple) crystalline precipitate consisting of mixed crystals of $(Zn(Hg(SCN)_4) + Cu[Hg(SCN)_4])$ is formed.



Place 1-2 drops of the prepared test solution of $Zn(II)$ in dilute acetic acid on a spot plate

add 1 drop of very dilute ($\sim 0.02M$) copper sulfate solution and 2 drops of ammonium mercuriothiocyanate reagent. Stir with a glass rod. A violet (or blackish purple) precipitate appears if $Zn(II)$ is present.

Alternatively, take 1-2 ml of the prepared test solution for testing of $Zn(II)$ in a semi-micro test tube add 1 drop of dilute copper sulfate solution ($\sim 0.02M$) and a few drops of ammonium mercuriothiocyanate reagent. Shake and scratch the sides of the test tube with a glass rod. A violet precipitate soon appears if $Zn(II)$ is present.

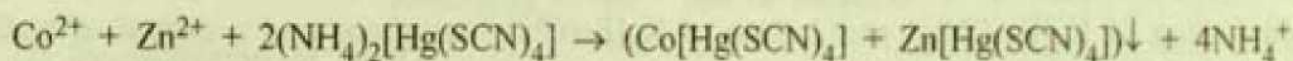
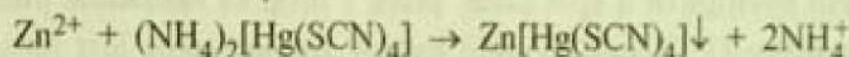
Add ~ 0.5 ml of iso amyl alcohol and shake. The violet precipitate collects at the interface between the aqueous and organic layers.

Fe^{III} may interfere by forming a blood red colouration, but it may be masked as $[FeF_6]^{3-}$ complex by adding a crystal of NH_4F or NH_4HF_2 to the test solution.

Limit of dilution: $1 : 1 \times 10^4$

(2) Ammonium mercuriothiocyanate-Cobalt nitrate reagent

$Zn(II)$ salts react with $(NH_4)_2[Hg(SCN)_4]$ reagent and give white precipitate of $Zn[Hg(SCN)_4]$. Cobalt (II) salts when react with $(NH_4)_2[Hg(SCN)_4]$, form a blue precipitate of $Co[Hg(SCN)_4]$, but the reaction takes about 2-3 minutes time. When small amount of $Zn(II)$ is present along with $Co(II)$, a blue precipitate is immediately formed, due to coprecipitation of $Co[Hg(SCN)_4]$ on $Zn[Hg(SCN)_4]$.



Fe^{III} , if present, forms a blood red colouration with SCN^- ion. On adding a crystal of NH_4F or NH_4HF_2 to the test solution Fe^{III} is masked as $[FeF_6]^{3-}$ complex ion and the blood red colour is discharged.

Place 1 drop of dilute cobalt nitrate solution on two adjacent cavities of a spot plate. Add 2 drops of ammonium mercuriothiocyanate reagent to each of the two cavities. Add 1 drop of the prepared test solution to one of the cavities and one drop of water to the other. Stir with two separate glass rods. If $Zn(II)$ is present, the blue precipitate comes almost immediately after addition of the test solution. The other cavity (blank) requires much more time ($\sim 2-3$ minutes) to form a blue precipitate.

Limit of identification: 0.2γ of Zn

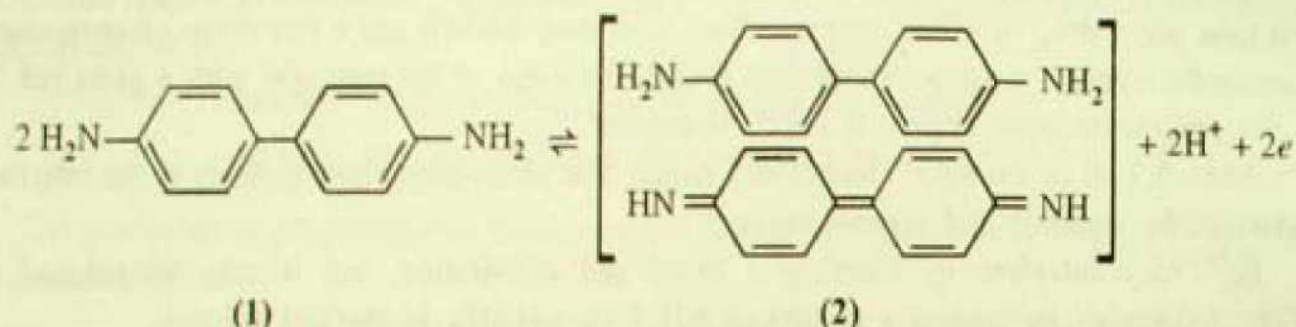
Limit of dilution: $1 : 2.5 \times 10^5$

(3) Ferrocyanide-ferricyanide-benzidine blue test

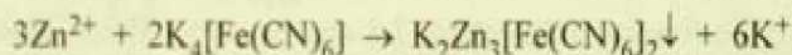
Reagent:

- Benzidine : Dissolve 0.05g of benzidine base or benzidine acetate in 10 ml of acetic acid and dilute to 100 ml with water and filter if necessary.
- Potassium ferricyanide (0.033 M): Dissolve ~ 1 g of $K_3[Fe(CN)_6]$ in water and dilute to 100 ml.
- Potassium ferrocyanide (0.033 M): Dissolve ~ 1 g. of $K_4[Fe(CN)_6] \cdot 3H_2O$ in water and dilute to 100 ml. Keep away from light.

E° value of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ redox couple is 0.36 volt. As such, $[\text{Fe}(\text{CN})_6]^{3-}$ can not oxidize benzidine (1) to benzidine blue (2) which is a meriquinoid oxidation product consisting of 1:1 mixture of the diamine (1) and its conjugate dimine (cf. p.250).



If Zn^{2+} ion is added to an (1:1) equilibrium mixture of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and $\text{K}_4[\text{Fe}(\text{CN})_6]$, the formal potential of $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ couple increases (cf. Sect. 2.4) and becomes sufficiently higher than that of the benzidine-benzidine blue redox couple, because of removal of $[\text{Fe}(\text{CN})_6]^{4-}$ ions from the system due to precipitation of sparingly soluble $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.



As a result, benzidine is oxidized to benzidine blue by ferricyanide $[\text{Fe}(\text{CN})_6]^{3-}$ ion.

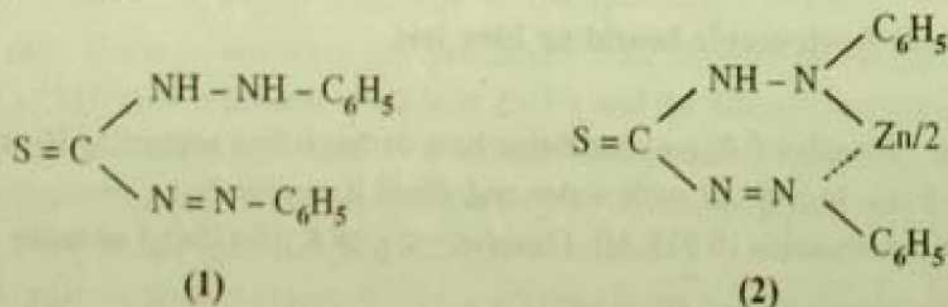
On two adjacent cavities of a spot plate, place 1 drop of benzidine plus 1 drop of methyl red indicator. Add drops (1:1) *aq*- NH_3 until methyl red indicator just turns yellow coloured. Add 1 drop of $\text{K}_3[\text{Fe}(\text{CN})_6]$ and 1 drop of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solutions and a crystal of sodium acetate to each cavity. Now add 1 drop of the prepared test solution of $\text{Zn}(\text{II})$ in dilute acetic acid to one of these cavities and a drop of distilled water to the other. A blue colouration appears almost at once in the test cavity if $\text{Zn}(\text{II})$ is present in the test solution.

Metals such as iron, copper, [uranium, molybdenum]* which form coloured precipitates or colourations with ferrocyanide and ferricyanide ions and oxidizing agents that may oxidize benzidine to benzidine blue must be absent.

(4) Dithizone (diphenylthiocarbazone) reagent

Reagent (0.005%): Dissolve 5 mg of dithizone in 100 ml of ethanol.

In acetic acid medium, dithizone (1) reacts with Zn^{2+} ion to form a red coloured innermetallic complex (2), which may be extracted into chloroform, imparting a red colour to the organic layer.



*Rare elements

Cu^{2+} , Hg_2^{2+} , Hg^{2+} , Ag^+ , Pd^{2+} , Au^{3+} , Pb^{2+} interfere. Except Pb^{2+} , interference due to the other metal ions may be eliminated if the test is carried out with NaOH extract of the sample, which contains Zn^{2+} as ZnO_2^{2-} and Pb^{2+} as PbO_2^{2-} . The other metal ions are precipitated as their hydroxides. Subsequent treatments of the NaOH extract with BaCl_2 and sodium sulfate solutions precipitate phosphate if any as $\text{Ba}_3(\text{PO}_4)_2$ and or $\text{Pb}_3(\text{PO}_4)_2$ and excess Ba^{2+} and Pb^{2+} as BaSO_4 and PbSO_4 respectively, which may be removed by centrifugation. The centrifugate after acidification with acetic acid may be tested for Zn^{2+} (call this as the prepared solution of Zn^{2+}).

To 1 ml of the prepared solution of Zn^{2+} in a semi-micro test tube, add 1 drop of the dithizone reagent, 0.5 ml of chloroform and shake. The organic layer assumes a red colour if Zn^{2+} is present. This test is now a characteristic of Zinc (II) only.

Limit of identification : 0.025γ of Zn

Limit of dilution: 1 : 6×10^7

4.18 Reactions of Barium (Ba^{II})

Indication

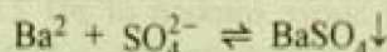
(1) Flame test

Yellowish-green (apple-green) flame. If BaSO_4 is suspected, flame test should be applied after reducing the sulfate to sulfide by holding the sample at the tip of a Pt-wire in the reducing flame.

Reactions of Ba^{2+} ion in solution

(1) Precipitation of BaSO_4

To 1 ml of the dil.HCl solution of the sample add 1 ml of dil. H_2SO_4 or 1 ml of a saturated solution calcium sulfate and shake. Heavy white precipitate of BaSO_4 appears.



Note

- (i) Sr^{2+} and Pb^{2+} also form similar white precipitates due to SrSO_4 and PbSO_4 respectively.
- (ii) On boiling with ammonium acetate, the precipitate of PbSO_4 passes into solution. (Difference from Ba^{2+} and Sr^{2+}).

(2) Precipitation of barium carbonate (BaCO_3)

To 1 ml of the test solution add 1 ml of saturated ammonium carbonate solution and a few drops of aq- NH_3 to render the solution ammoniacal. White precipitate of BaCO_3 appears.



The precipitate of BaCO_3 is soluble in dil.acetic acid and dil. mineral acids (HCl , HNO_3).

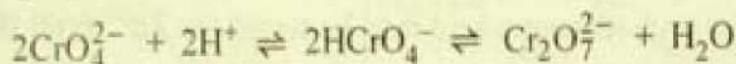
(3) Precipitation of BaCrO_4

To 1 ml of the neutral test solution add 1 ml of saturated potassium chromate solution and shake. Yellow precipitate of BaCrO_4 ($pK_{sp} \approx 9.8$) settles down.



The precipitate is insoluble in dilute acetic acid (distinction from CaCrO_4 and SrCrO_4), but soluble in dil.HCl or dil.HNO_3 . The precipitate is also insoluble in NaOH solution (distinction from PbCrO_4).

In presence of acid, CrO_4^{2-} ion disappears from the solution due to the formation of dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$):



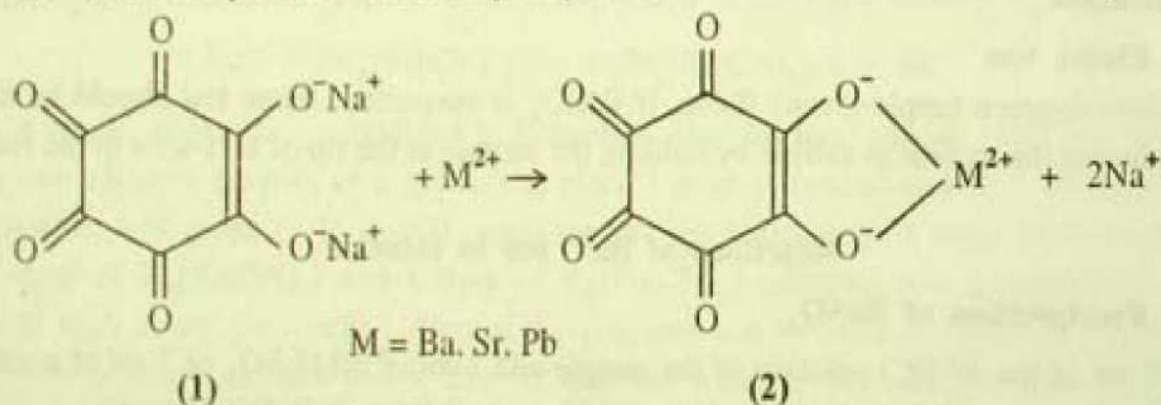
As a result, only BaCrO_4 ($pK_{sp} \approx 9.8$) is precipitated, not SrCrO_4 and CaCrO_4 which are more soluble than BaCrO_4 .

Confirmation

(1) Test with sodium rhodizonate

Reagent: 0.2% aqueous solution.

Yellow solution of sodium rhodizonate (1) reacts with neutral solution of divalent heavy metals (M^{2+}) ions to produce coloured precipitates of the metal rhodizonate complexes (2):



Pb^{2+} gives blue fleck or ring. In presence of buffer solution of $\text{pH } 2.8^*$, the precipitate turns scarlet. Ba^{2+} gives red-brown precipitate of barium rhodizonate which does not dissolve in dil.HCl . Sr^{2+} produces similar rhodizonate, but soluble in dil.HCl . Ca^{2+} does not form insoluble rhodizonate. Deep colours of the rhodizonates of these non-transition metal ions are due to the presence of five conjugated double bonds in the anionic ligand.

Place 1 drop of the neutral or weakly acidic test solution on a spot paper and dry it. Add 1 drop of the reagent using a capillary dropper. A redish-brown spot is obtained if Ba^{2+} is present.

Treat the redish brown spot of barium rhodizonate with 1 drop of 0.5 M HCl , a bright-red stain is formed if Ba^{2+} is present. If Ba^{2+} is absent, the spot disappears.

NB. (1) Filter paper strip impregnated with the reagent solution may be preserved in dark after drying it over $\text{conc.H}_2\text{SO}_4$ in vacuo. Otherwise, finely divided rhodizonate is decomposed oxidatively.

(2) It is convenient to precipitate BaCO_3 , SrCO_3 , CaCO_3 by treating the test solution with ammonium carbonate in presence of NH_4Cl . Since BaCO_3 is more soluble than CaCO_3 and

*Dissolve 1.9 g of sodium hydrogen tartarate and 1.5 g of tartaric acid in water and dilute to 100 ml.



SrCO_3 , if the precipitate is thoroughly washed and treated with sodium rhodizonate solution, a redish-brown precipitate is formed if Ba^{2+} is present. CaCO_3 and SrCO_3 do not react under this condition.

Limit of identification: 0.25 γ of Ba

Limit of dilution: 1 : 2×10^5

(2) Detection of Ba^{2+} in presence of Sr^{2+}

Precipitate carbonates of Ba^{2+} and Sr^{2+} by treating 1 ml of the test solution with 1 ml of saturated $(\text{NH}_4)_2\text{CO}_3$ solution. Wash twice by centrifugation. Place ~0.1 mg of the washed precipitate of the carbonate mixture on a cavity of a spot plate, add 1 drop of 0.2% sodium rhodizonate solution and stir with a glass rod. If the precipitate turns brownish-red, Ba^{2+} is present. If brownish-red colouration of the precipitate is not observed, add 1 drop of dil.acetic acid (~1N) and stir with a glass rod. If a red precipitate or colouration appears, Ba^{2+} or Sr^{2+} or both are indicated.

(3) Detection of Ba^{2+} and Sr^{2+}

Place 1 drop of 0.5% solution of sodium rhodizonate reagent on a spot paper (Whatman No. 1) and dry the paper. A yellow spot is formed. Add a drop of the neutral or weakly acidic test solution at the centre of the reagent spot using a capillary dropper. If Ba^{2+} or Sr^{2+} or both are present a brownish-red spot is formed. To the resulting spot, add 1-2 drops of a 1:1 mixture of a saturated solution of dimethylamine hydrochloride $[(\text{H}_3\text{C})_2\text{NH}.\text{HCl}]$ in water and 95% ethanol. In presence of Ba^{2+} , the colour of the spot changes to bright red. If Sr^{2+} is present, the red-brown spot gradually transforms to blue-violet.

If both Ba^{2+} and Sr^{2+} are present, the bright red spot due to Ba-rhodizonate becomes encircled by a blue-violet ring of Sr-rhodizonate, which migrates to the periphery along with the reagent.

Limit of identification : 0.5 γ of Ba

Limit of dilution : 1 : 1×10^5

(4) BaSO_4 - KMnO_4 mixed crystal formation

When BaSO_4 precipitate is formed in presence of KMnO_4 , pink coloured mixed crystals of BaSO_4 - KMnO_4 settles down. Due to the absence of free MnO_4^- ion, the pink colour of the micro crystals are not affected by reducing agents, viz, H_2O_2 , oxalic acid, Fe^{II} salt, SO_2 -water etc.

To 1 drop of the test solution in a small centrifuge tube add 3 drops of cold, saturated KMnO_4 solution and a few drops of dil. H_2SO_4 . Stir the mixture with a glass rod, centrifuge and remove the centrifugate using a capillary dropper. Add a few drops of SO_2 -water or H_2O_2 . The violet colour of the supernatant solution is discharged but the purple colour of the BaSO_4 - KMnO_4 precipitate is distinctly visible against a white back ground. It is better seen using a magnifying glass.

Limit of identification: 5 γ of Ba

Limit of dilution: 1 : 1×10^4

4.19. Reactions of Strontium (Sr^{II})

Indication

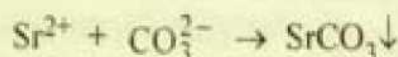
(1) **Flame colouration** : Carmine-red colour to the non-luminous flame.

Reactions of Sr^{2+} ion in Solution

(1) White precipitate of SrSO_4 on treatment of the neutral or weakly acidic test solution with $\text{dil. H}_2\text{SO}_4$.



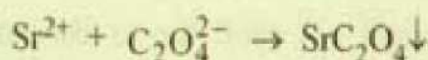
(2) White precipitate of SrCO_3 on treatment of the neutral test solution with saturated $(\text{NH}_4)_2\text{CO}_3$ solution in presence of NH_4Cl and aq-NH_3 .



(3) White precipitate of SrSO_4 appears on treatment of the neutral or weakly acidic test solution with saturated CaSO_4 solution. The precipitate of SrSO_4 on boiling with conc. solution of Na_2CO_3 , is transformed into SrCO_3 as the solubility product of SrCO_3 ($pK_{sp} = 9.96$) is less than that of SrSO_4 ($pK_{sp} = 6.6$).



(4) White precipitate of Sr-oxalate, SrC_2O_4 appears on addition of saturated ammonium oxalate and aqueous - NH_3 to a neutral or weakly acidic test solution containing Sr^{2+} .



(5) Test with K_2CrO_4

To 1 ml of the neutral test solution in a semi-micro test tube, add 1 ml of saturated K_2CrO_4 solution. Yellow precipitate of SrCrO_4 settles down immediately. Add a few drops of acetic acid, the precipitate passes into solution (distinction from Ba^{2+} , since BaCrO_4 is not soluble in acetic acid).

Confirmation

(1) Sodium rhodizonate solution

Reagent: 0.2% solution of sodium rhodizonate.

Since both Ba^{2+} and Sr^{2+} respond to this test forming redish-brown precipitate, so the test may be applied for detection of Sr^{2+} only after removing Ba^{2+} , as BaCrO_4 by treating the neutral test solution with a saturated solution of K_2CrO_4 . Sr^{2+} is also precipitated as SrCrO_4 , but unlike BaCrO_4 ($pK_{sp} = 9.93$), it is appreciably soluble in water ($pK_{sp} \sim 4.65$) and also in dil. acetic acid.

Place 1 drop of the test solution on a drop reaction paper impregnated with saturated K_2CrO_4 solution, when yellow spot due to chromates of the metal ions present in the test solution are



formed on the paper. Dry the paper. Add 1 drop of an 0.2% aqueous solution of sodium rhodizonate on the yellow spot. A brownish-red flake or a ring is formed if Sr^{2+} is present.

Limit of identification : 3.9% of Sr,

Limit of dilution : 1 : 12,800, in presence of 80 times the amount of Ba.

4.20. Reactions of Calcium (Ca^{II})

Indication

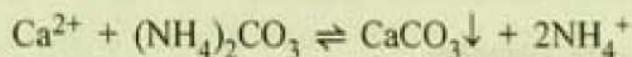
(1) Flame colouration

Transient yellowish red (brick-red) colouration is imparted on the non-luminous Bunsen flame, if Ca^{2+} is present. If SO_4^{2-} is suspected, flame test is to be applied after reducing SO_4^{2-} to S^{2-} . For this purpose, moisten the Pt-wire with conc.HCl and adhere a small amount of the sample to it. Hold the tip of the Pt-wire containing the sample in the reducing zone of the Bunsen burner for a few minutes (*cf.* Fig. 6.1). Unburnt carbon, present in the reducing flame, reduces SO_4^{2-} to S^{2-} . Moisten the Pt-wire again with conc.HCl and hold the same in the non-luminous zone of the burner and observe the colouration. Repeat the whole operation in a number of times before making the final conclusion.

Reactions of Ca^{2+} ion in solution

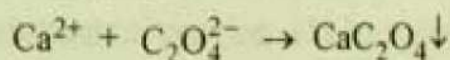
(1) Precipitation with ammonium carbonate solution

To 1 ml of the neutral test solution add 1 ml of saturated $(\text{NH}_4)_2\text{CO}_3$ solution. White precipitate of CaCO_3 appears. Ba^{2+} and Sr^{2+} also give similar precipitates.



(2) White precipitate with ammonium oxalate

To 1 ml of the neutral or weakly acidic test solution add 1 ml of saturated ammonium oxalate solution and a few drops of aq- NH_3 to render the solution ammoniacal. White precipitate of calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) appears.



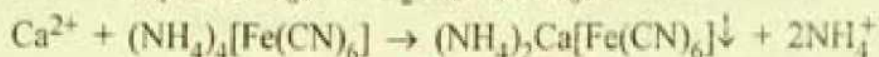
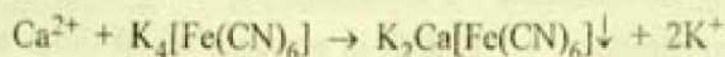
The precipitate is insoluble in acetic acid, but soluble in mineral acids (HCl , HNO_3).

Confirmation

These tests should be conducted with the precipitate of carbonates (of Ca^{2+} , Sr^{2+} , Ba^{2+} if present) obtained on treatment of the neutral test solution with ammonium carbonate solution. Dissolve the precipitate of carbonates in dil. acetic acid and perform the following tests.

(1) Test with potassium ferrocyanide or ammonium ferrocyanide solution (0.025 M)

Ca^{2+} forms insoluble mixed K^+Ca^{2+} - ferrocyanide or $\text{NH}_4^+\text{Ca}^{2+}$ - ferrocyanide when treated with these reagents.



Ca^{2+} may be distinguished from Sr^{2+} by this test, but Mg^{2+} and Ba^{2+} interfere. Unlike these mixed ferrocyanides, pure alkali or alkaline earth metal ferrocyanides are soluble in water.

Place a drop of the test solution on a small watch glass and add a few drops of ammonium ferrocyanide (or potassium ferrocyanide and ammonium chloride solutions). Add 1-2 drops of ethanol to this mixture and stir with a glass rod. In presence of Ca^{2+} , a crystalline precipitate (or cloudiness) of mixed ferrocyanides appears. The precipitate may be clearly visible on placing the watch glass on a glazed black paper.

Limit of identification : 25% of Ca

Limit of dilution : 1 : 2500 (on watch glass), 1 : 1×10^6 (in micro test tube).

(2) Microscopic test on calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$)

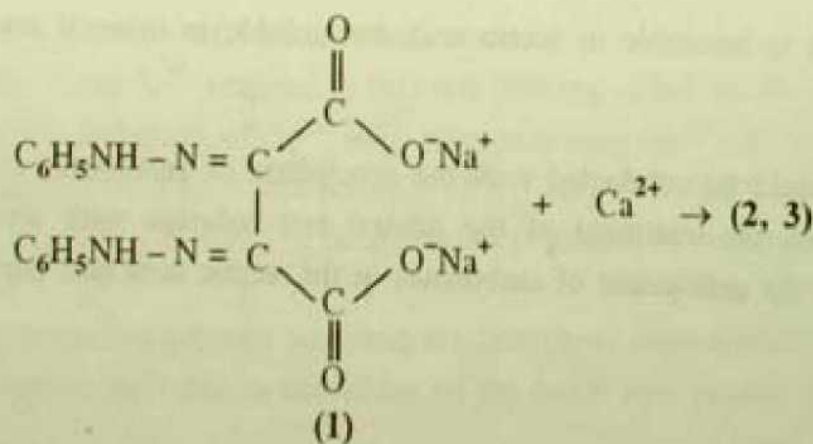
Take a few drops of the test solution on a watch glass and place the same on a hot water bath. Evaporate the solution to dryness and then dissolve the residue in 1-2 drops of water. Transfer the solution to a microscope slide and add a minute drop of dil. H_2SO_4 using a capillary dropper. If no precipitate is formed, warm the slide on the hot water bath until crystallization starts at the edges. Examine the crystals with a microscope (magnification 110 $\times$). Bundles of needle shaped or elongated prism like crystals will be visible if Ca^{2+} is present.

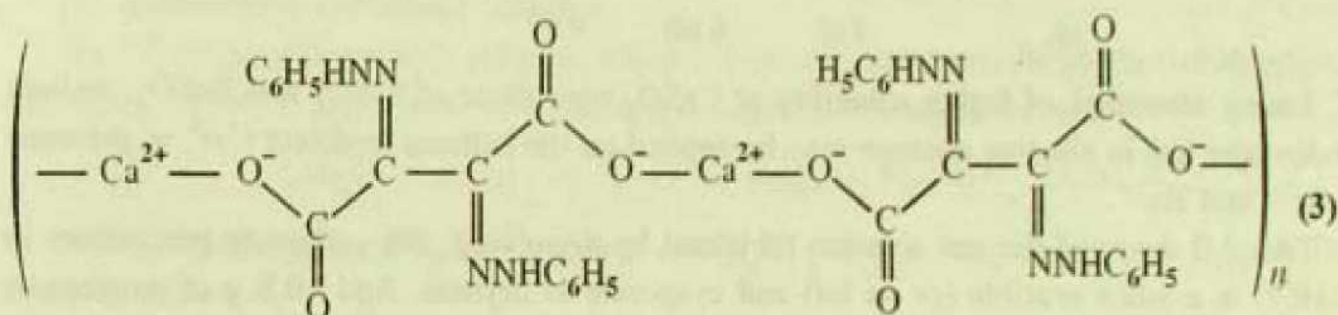
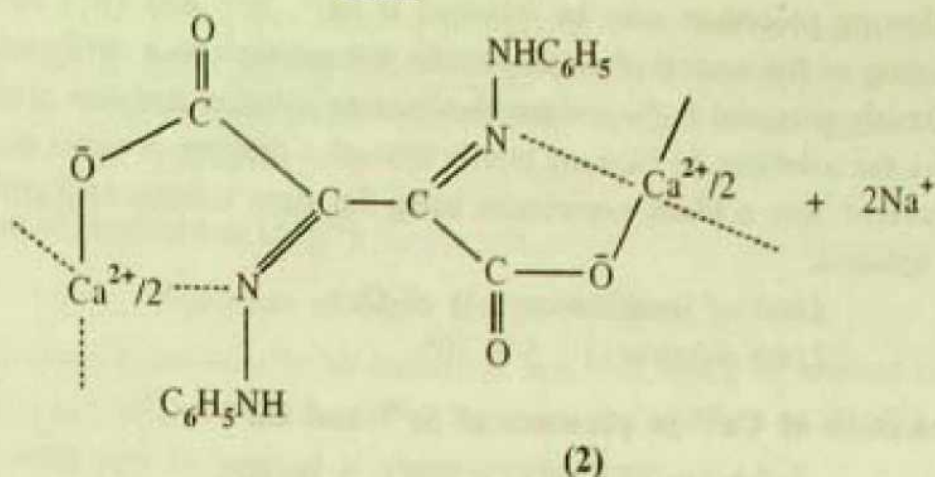
Limit of dilution: 1 : 6000.

(3) Sodium dihydroxytartarate osazone

(i.e, Na-salt of succinic acid-dioxo-2, 3 - bis phenylhydrazone) reagent

Aqueous solution of the sodium salt of the osazone of dihydroxytartaric acid (1) forms bright yellow flocculent precipitate with alkaline earth metal ions. The reagent is specific for Ca^{2+} if metal ions except Na^+ , K^+ , and NH_4^+ ions are absent. Small quantity of Mg^{2+} does not interfere. The solid reagent provides a very sensitive test for Ca^{2+} . Although various structures may be written for the metal complexes of (1), polymeric structures (2 and 3) appear more likely.





Place 1 drop of the neutral test solution on a small watch glass and add several grains of the reagent powder to it. Stir with a glass rod. Place the watch glass on a black paper. The reagent dissolves completely within a few minutes. Initially a fine skin like appearance covers the drop and finally a dense yellow precipitate is formed depending upon the amount of Ca^{2+} present.

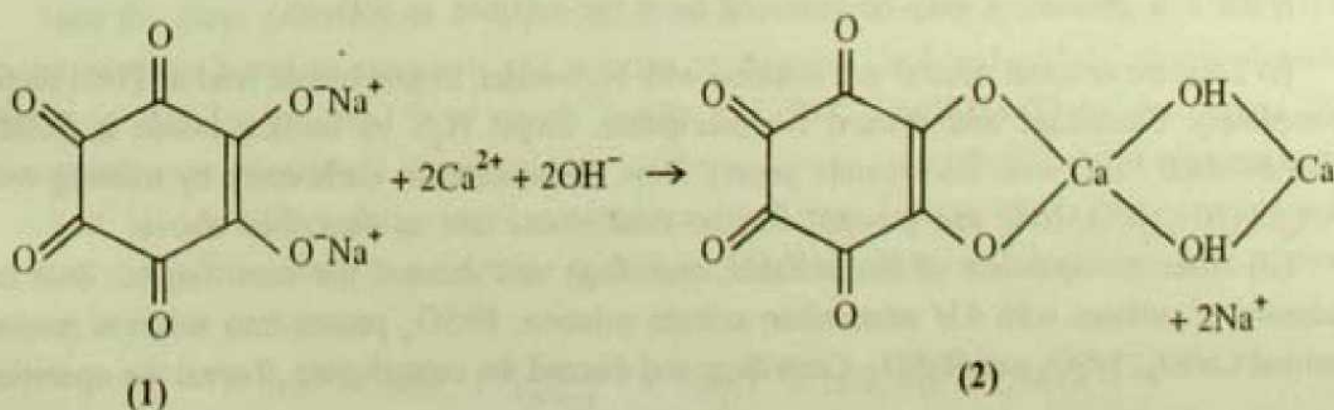
Run a blank experiment with distilled water instead of the sample solution.

Limit of identification: 0.01γ of Ca

Limit of dilution: 1 : 5×10^6

(4) Test with sodium rhodizonate reagent

Neutral solution of Ca^{2+} does not form any precipitate with sodium rhodizonate (1), but in basic solution, a violet precipitate is formed due basic calcium rhodizonate (2). Calcium sulfate responds to this test due to its higher solubility than barium and strontium sulfates. However, the test can not be applied with CaCO_3 . On the other hand, BaCO_3 responds to this test due to its higher solubility than CaCO_3 .





The following procedure may be followed if Ba^{2+} , Sr^{2+} and Pb^{2+} salts are absent.

Place a drop of the neutral or weakly acidic test solution on a cavity of a spot plate. Add a drop of freshly prepared 0.2% sodium rhodizonate solution and one drop of 0.5 M NaOH solution. Mix the solutions by blowing briefly through a dropper. A violet precipitate is formed if Ca^{2+} is present. Run a blank experiment using the same volume of distilled water in place of the test solution.

Limit of identification : 1γ of Ca

Limit dilution: $1 : 5 \times 10^4$

(4a) Detection of Ca^{2+} in presence of Sr^{2+} and Ba^{2+}

Solubility of $\text{CaSO}_4 > \text{SrSO}_4 > \text{BaSO}_4$

pK_{sp} 4.62 6.60 9.97

Taking advantage of higher solubility of CaSO_4 over those of SrSO_4 and BaSO_4 , sodium rhodizonate test in alkaline medium may be applied on the sulfates to detect Ca^{2+} in presence of Sr^{2+} and Ba^{2+} .

Take 1-2 drops of the test solution (obtained by dissolving the carbonate precipitates in dil.HCl) in a silica crucible (or its lid) and evaporate to dryness. Add ~0.5 g of ammonium sulfate and heat the mixture inside a **FUME CUPBOARD** initially gently and finally strongly to drive off the white fumes due to ammonium sulfate completely. Cool the mass and treat it with a drop of 0.2% sodium rhodizonate solution and a drop of 0.5 M NaOH solution. In presence of Ca^{2+} , the white precipitate of sulfate is tinted more or less violet.

Large quantities of Ba^{2+} does not interfere. SrSO_4 in mixture with $\text{BaSO}_4/\text{CaSO}_4$ may be detected by this technique using a neutral solution of sodium rhodizonate, when a violet colouration is observed.

The following comparison maybe useful in studying the properties of CaSO_4 , SrSO_4 and BaSO_4 towards neutral and basic solution of sodium rhodizonate:

	Na-rhodizonate (neutral)	Na-rhodizonate + 0.5 M NaOH (basic)
CaSO_4	No response	Positive test (violet precipitate)
SrSO_4	Positive test (violet colouration)	No response
BaSO_4	No response	No response

If Pb^{2+} is present, it may be removed from the mixture as follows:

(i) Treat the original neutral test solution with H_2S -water, to precipitate lead as PbS (black) completely. Centrifuge and discard the precipitate. Expel H_2S by boiling inside a **FUME CUPBOARD** (test with lead-acetate paper). Now, precipitate the carbonates by treating with $\text{NH}_4\text{Cl}-(\text{NH}_4)_2\text{CO}_3-\text{NH}_3$ and proceed for the rhodizonate test as described above.

(ii) After precipitation of the sulfates, centrifuge and discard the centrifugate. Boil the mixture of sulfates with 6M ammonium acetate solution. PbSO_4 passes into solution leaving behind CaSO_4 , SrSO_4 and BaSO_4 . Centrifuge and discard the centrifugate. Repeat the operation

to remove lead completely (until the centrifugate does not form any yellow precipitate with 5% K_2CrO_4 solution). Wash the precipitate with water by repeated centrifugation. Proceed as before for the rhodizonate test.

4.21 Reactions of Magnesium (Mg^{II})

Reactions of Mg^{2+} ion in Solution

For Magnesium there is practically no indicative test, that could be applied on the solid samples. However, some indicative tests may be applied to the aqueous or dil.HCl solution of Mg^{2+} salts. These tests may be applied if phosphate is absent.

(1) Ammonium carbonate solution

To 1-2 drops of the sample solution, add 2-3 drops of ammonium carbonate ($\sim 1M$) solution and shake. A white precipitate of basic magnesium carbonate is formed.



Now perform the same test in presence of NH_4Cl ($\sim 0.1g$). No precipitate is formed. Due to the equilibrium,



concentration of CO_3^{2-} ion is depressed and the solubility product of the precipitate is not exceeded [pK_{sp} of pure $MgCO_3 = 5$]

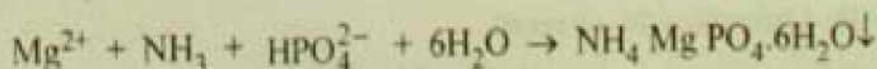
(2) Phosphoric acid-Oxalic acid-Sulfuric acid (POS) reagent

This reagent may be added to remove the metal ions other than Mg^{2+} from the test solution.

To 1-2 ml of the test solution in a semi-micro test tube, add equal volume of the reagent solution. If Fe^{II} is present oxidize it to Fe^{III} by adding a few drops of H_2O_2 or Br_2 -water. Neutralize the solution with 1:1 aqueous- NH_3 solution to a just yellow and then to just red of methyl red indicator with very dilute HCl. Add an equal volume of ammonium acetate-acetic acid buffer ($pH \sim 4-5$) and boil gently for 2 minutes. Cool, centrifuge and reject any precipitate at this stage.

Note: At this stage metal ions which form sparingly soluble phosphates at pH (4-5) and those form insoluble sulfates and oxalate, if present, are precipitated.

Take the clear centrifugate in a porcelain basin or in a semi-micro beaker (10 ml). Heat on an asbestos board to evaporate the solution to dryness. Cool and add 1-2 drops of conc. HNO_3 to the dry residue. Heat gently inside a **FUME CUPBOARD** to decompose the ammonium salts completely. Cool and take up the residue if any with 1-2 drops of water. Add drops of 1:1 aq- NH_3 solution until ammoniacal and then 1 drop of Na_2HPO_4 solution if necessary. White crystalline precipitate of $NH_4MgPO_4 \cdot 6H_2O$ appears on stirring with a glass rod, if Mg^{2+} is present,



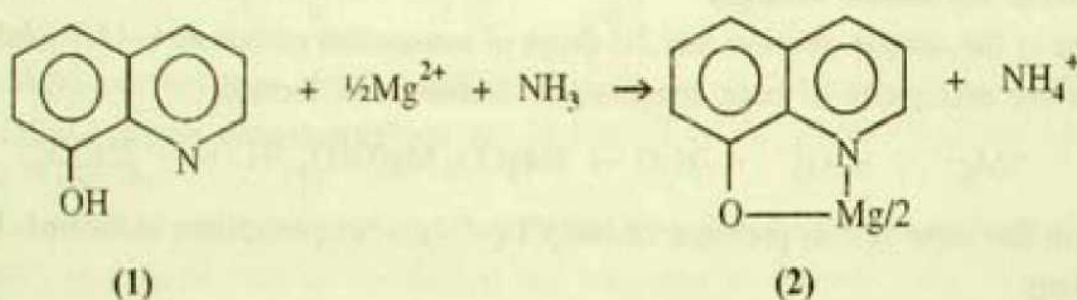
Confirmation

These tests may be applied directly on the aqueous extract obtained after removal of other metal ions by the POS reagent and decomposition of the ammonium salts by heating with HNO_3 .

(1) 8-Hydroxyquinoline (Oxine) reagent

Reagent: 2% solution of the reagent in acetic acid.

To 1 ml of the test solution add a pinch (<0.1 g) of NH_4Cl and heat to boiling. Add 1-2 drops of the oxine reagent (1) solution and sufficient (1:1) aq- NH_3 to render the solution ammoniacal. Heat to boiling. A yellow precipitate of magnesium oxinate (2) $\text{Mg}(\text{C}_9\text{H}_6\text{ON})_2 \cdot 4\text{H}_2\text{O}$ appears.

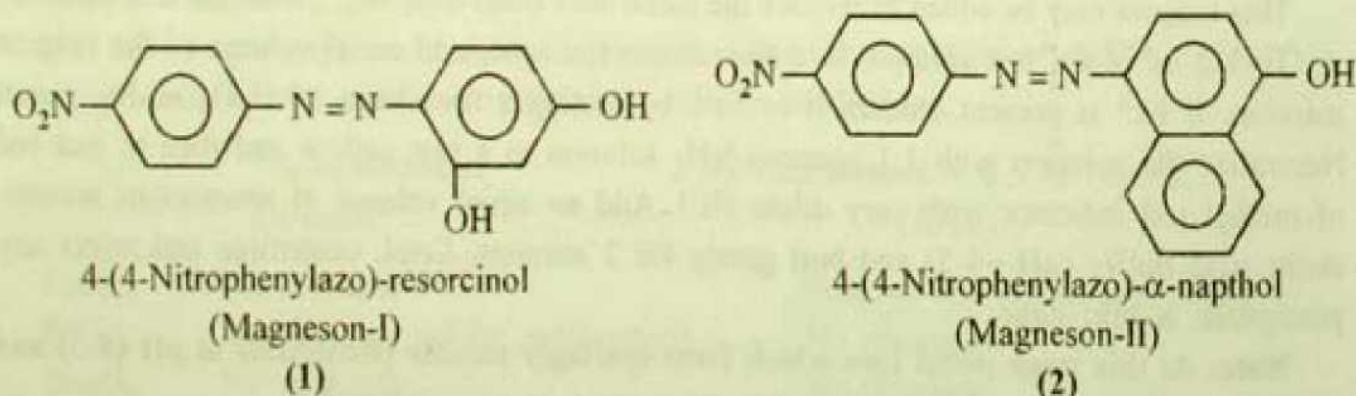


Note: Metal ions other than Na^+ and K^+ must be absent.

(2) Test with Magneson-I or Magneson-II reagent

Reagent: 0.001 g of the dye (Magneson I or II) is dissolved in 100 ml of 2 M NaOH solution.

The Magneson reagents (1 and 2) are:



Both these azo dyes are red to red-violet coloured in alkaline solution. These are adsorbed by precipitated $\text{Mg}(\text{OH})_2$ to produce deep blue adsorption products.

Place 1-2 drops of the test solution in a spot plate, add 1-2 drops of NaOH (~2M) solution and 1 drop of the alkaline solution of the reagent (Magneson-I or Magneson -II). According to the Mg^{2+} content, a blue precipitate or a colour change from red-violet to blue is observed.

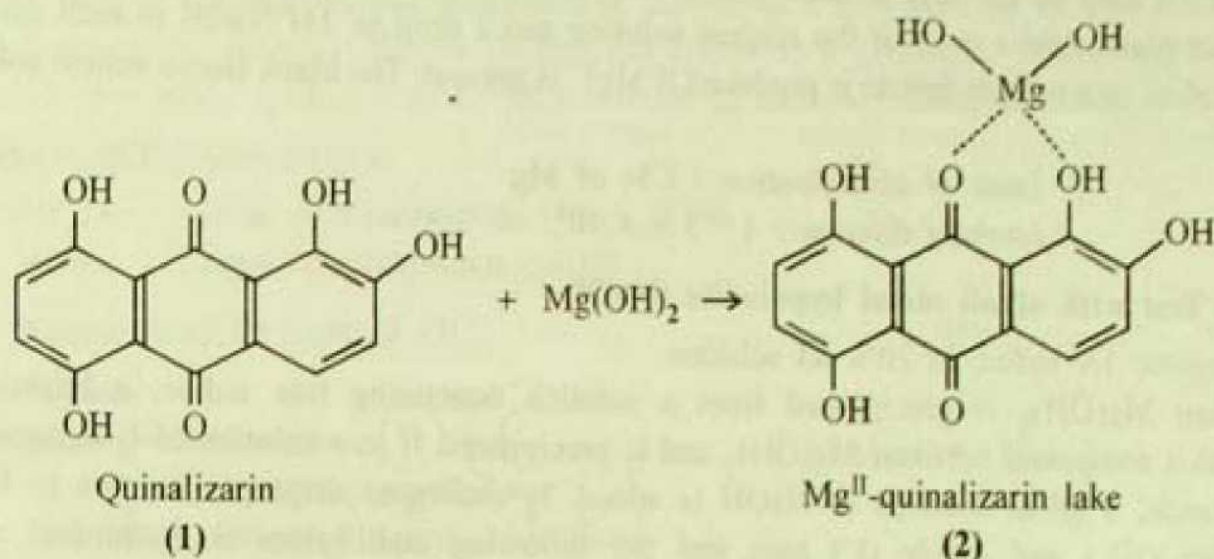
Limit of identification: (γ of Mg): 0.5 (with 1) and 0.19 (with 2)

Limit of dilution : 1 : 1×10^5 (with 1) and 1 : 2.6×10^5 (with 2)

(3) Test with Quinalizarin reagent

Reagent: 0.05% solution in NaOH or 0.01-0.02% solution in ethanol.

Alkaline solution of quinalizarin (1, 2, 5, 8 - tetrahydroxyanthraquinone, 1) forms a blue precipitate or cornflower blue colouration with magnesium hydroxide.



The coloured product (2) is a magnesium hydroxide-quinalizarin lake (an adsorption compound of $\text{Mg}(\text{OH})_2$ and the dye stuff).

Note: Alkaline earth metals and aluminium, phosphate and metal ions forming sparingly soluble phosphates in alkaline medium should be absent. Large amount of ammonium salts decrease the sensitivity of the test.

Place a drop of the test solution and a drop of distilled water in two adjacent cavities of a spot plate. Add 2 drops of the quinalizarin reagent solution to each cavity. If the test solution is acidic, a yellowish-red colour appears. Add drops of 2M NaOH until the colour changes to violet, and then a few drops more. A blue precipitate or colouration appears if Mg^{2+} is present. The blank shows a blue-violet colour.

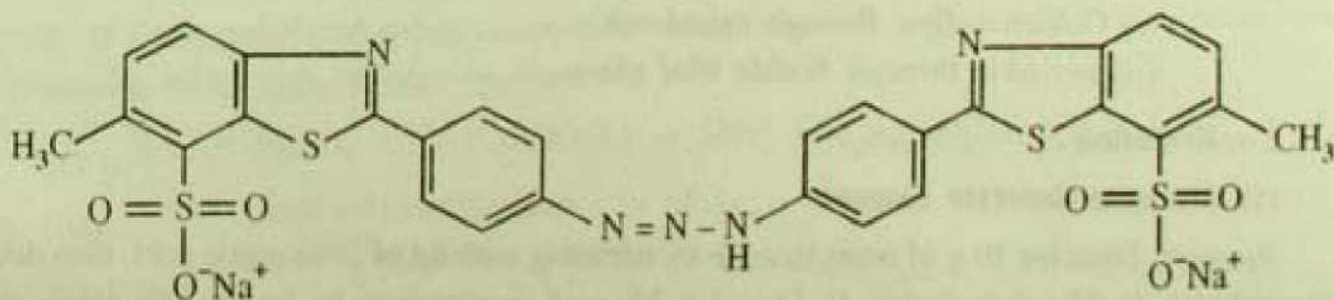
Limit of identification: 0.25γ of Mg

Limit of dilution : 1 : 2×10^5

(4) Titan yellow test

Reagent: 0.1% solution in water.

$\text{Mg}(\text{OH})_2$ forms a deep red coloured adsorption product with the water soluble dye stuff, thiazole yellow-G (*titan yellow*). Depending upon the amount of Mg^{2+} , a deep-red colour or a red precipitate is formed.



Titan yellow

N.B.: Ba^{2+} and Ca^{2+} do not form any precipitate with the reagent, but only intensify its colour. Elements, forming sparingly soluble sulfides and phosphates should be absent.

Place a drop of the test solution and a drop of distilled water on two adjacent cavities of a spot plate. Add a drop of the reagent solution and a drop of $2M$ NaOH to each cavity. A red colour or a red precipitate is produced if Mg^{2+} is present. The blank shows yellow colour only.

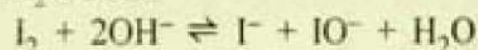
Limit of identification : 1.5γ of Mg

Limit of dilution : $1 : 3.3 \times 10^4$

(5) Test with alkali metal hypoiodite (NaOI)

Reagent: $1N$ iodine in 20% KI solution.

When $\text{Mg}(\text{OH})_2$ is precipitated from a solution containing free iodine, a brown-red adsorption compound between $\text{Mg}(\text{OH})_2$ and I_2 precipitates. If to a solution of I_2 in aqueous KI solution, a dilute solution of NaOH is added, I_2 undergoes disproportionation to form hypiodite (IO^-) and iodide (I^-) ions and the following equilibrium is established with decolourization of I_2 colour:



If this decolourised IO^-/I^- equilibrium mixture is treated with a Mg^{2+} salt solution, OH^- ions are removed from the solution due to precipitation of $\text{Mg}(\text{OH})_2$ and the above equilibrium shifts to left liberating iodine which forms a brown-red adsorption compound with precipitated $\text{Mg}(\text{OH})_2$.

Place 1 drop of the neutral or weakly acidic test solution on a spot plate and add one micro drop of $\sim 1M$ KOH or NaOH or saturated lime-water using a capillary dropper, followed by a micro drop of iodine solution. Stir the mixture with a glass rod. The solution should be brown. Add more iodine solution if necessary. Wait for 1 minute and add more alkali solution until the solution becomes lemon yellow. In presence of Mg^{2+} , brown flakes of $\text{I}_2 \dots \text{Mg}(\text{OH})_2$ adsorption compound will be clearly visible in the yellow solution. Run also a blank test.

Limit of identification: 0.3γ of Mg .

Limit of dilution: $1 : 1.65 \times 10^5$

4.22 Reactions of Sodium (Na^+)

Indication

(1) Flame colouration

- (i) Golden yellow through naked eye.
- (ii) Invisible through double blue glass.

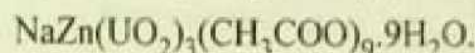
Confirmation

(1) Zincuranylacetate reagent

Reagent: Dissolve $10g$ of uranylacetate by warming with $6g$ of 30% acetic acid, then dilute the solution to $50ml$ (solution-A). Dissolve $30g$ of zinc acetate in $3g$ of 30% acetic acid by stirring and warming and then diluting to $50ml$ (solution-B). Mix solutions A and B and

warm gently to obtain a clear solution. Add a minute quantity of sodium chloride and stir. Cool the solution to room temperature and allow to stand for 24 hours. Filter through a Whatman No 42 filter paper. Use the filtrate for the tests. The reagent keeps indefinitely.

To a drop of the neutral clear test solution, placed on a spot plate or on a watch glass, add 8 drops of the zincuranylacetate reagent and stir with a glass rod. Yellow turbidity or crystalline precipitate appears, due to the formation of sodium zincuranylacetate,



Limit of identification: 12.5γ of Na

Limit of dilution : 1 : 4000

4.23. Reaction of Potassium (K^+)

Indication

(1) Flame colouration

- (i) Violet through nacked eye.
- (ii) Red through double blue glass.

Confirmation

(1) Sodium cobaltinitrite test

Place a drop of the neutral or acetic acid test solution on a spot plate, add a small amount of finely powdered sodium cobaltinitrite and stir with a glass rod. Yellow precipitate or turbidity due to potassium cobaltinitrite appears.



Interference: NH_4^+ ion gives similar precipitate. Ammonium salts, if present, should be removed by evaporating the solution to dryness and then heating the resulting dry mass with one drop of conc. HNO_3 in a **FUME CUPBOARD**. The resulting mass is to be taken up with water and neutralized with sodium acetate.

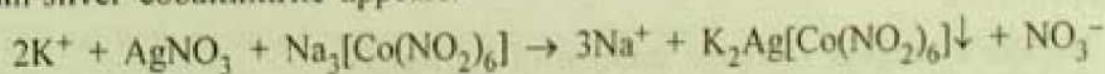
Limit of identification: 4γ of K

Limit of dilution: 1 : 12,500

(2) Sodium cobaltinitrite-Silver nitrate test

Note: This test is much more sensitive than the sodium cobaltinitrite test, but both ammonium salts and halide ions must be absent.

Place a drop of the neutral or acetic acid test solution on a spot plate and add a drop of 0.1 M silver nitrate solution. Centrifuge if any precipitate appears at this stage. Add a small amount of finely powdered sodium cobaltinitrite and stir with a glass rod. Yellow precipitate of potassium-silver cobaltinitrite appears.



Limit of identification : 1γ of Ag.

Limit of dilution : 1 : 50,000.

(3) Perchloric acid (HClO_4) or Sodium perchlorate (NaClO_4)

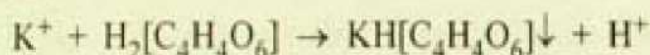
To 1-2 drops of the test solution in a test tube add one drop of dil. HClO_4 (~5M) or NaClO_4 (~1M) solution and shake. White crystalline precipitate of potassium perchlorate appears.



(4) Tartaric acid or sodium hydrogentartarate reagent

Potassium hydrogen tartarate is sparingly soluble.

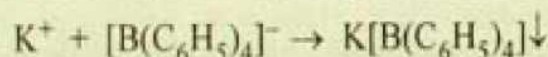
Take 2-3 drops of the test solution in a semi-micro test tube and add 2-3 drops of sodium hydrogen tartarate, or, a (1:1) mixture of tartaric acid (~1 M) and sodium acetate (~1 M). Add equal volume of ethanol and shake well. White crystalline precipitate of potassium hydrogen tartarate soon appears.



Ammonium salts yield a similar precipitate and must be removed by boiling with dil. NaOH solution.

5. Sodium tetraphenyl boron reagent

Place 1 drop of the neutral or dilute acetic acid test solution on a black spot plate or in a small watch glass kept on a black paper, add 2 drops of 2% aqueous solution of sodium tetraphenyl boron. White crystalline precipitate of potassium tetraphenyl boron soon appears.



The precipitate is soluble in strong acid, alkalies and also in acetone. NH_4^+ , Rb^+ , Cs^+ , Ti^+ salts interfere.

4.24. Reactions of Ammonium (NH_4^+)

Indication

(1) White sublimate in dry test tube heating test.

(2) NH_3 gas is evolved on heating the sample with solid Na_2CO_3 or strong NaOH solution in a test tube. If a filter paper strip, moistened with colourless phenolphthalin indicator solution is held above the mouth of the test tube, the paper turns red, due to basic nature of NH_3 gas (Fig. 3.27, 3.28, 3.29a 3.30b).



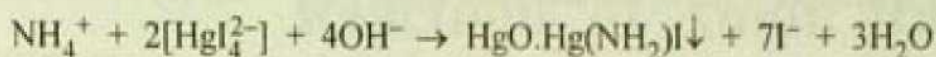
Confirmation

(1) Nessler's reagent (alkaline solution of $\text{K}_2[\text{HgI}_4]$).

Procedure-1

Mix a drop of the test solution with a drop of strong NaOH solution on a watch glass and transfer a drop of this reaction mixture (solution or suspension) to a spot test paper. Dry

the paper by holding it near a flame and add a drop of Nessler's reagent. A yellow to orange stain or ring is produced on the paper.



Interference: All metal ions except Na^+ and K^+ interfere and must be absent.

Procedure-2

Place a drop of the test solution or a small amount ($\sim 0.1\text{g}$) of the solid sample in a small test tube, add 1-2 drops of dil. NaOH solution ($\sim 2M$) and place the test tube in a hot water bath (Fig 3.1.5). Hold a small strip of filter paper spotted with a drop of Nessler's reagent inside the tube avoiding contact with the wall, using a hook made of a glass rod or a Pt-wire, for ~ 5 minutes (Fig 3.28a, 3.29a). The spot turns yellow.

Limit of identification : 0.3γ of NH_3

Limit of dilution: 1 : 6666

(2) Litmus test

Follow the procedure as above (Procedure-2) and hold a small piece of red litmus paper inside the tube (Fig. 3.28a, 3.29a). The litmus paper turns blue.

Limit of identification : 0.01γ of NH_3

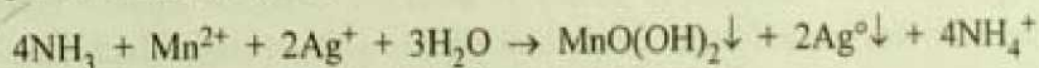
Limit of dilution: 1 : 5×10^6

(3) Phenolphthalin test

Follow the procedure as above (Procedure-2) and hold a filter paper strip moistened with colourless phenolphthalin indicator solution (Fig. 3.28a, 3.29a). The indicator spot turns red.

(4) MnSO_4 - AgNO_3 test

Follow the procedure as Procedure-2 above and hold a filter paper strip spotted with a drop of MnSO_4 - AgNO_3 reagent to the issuing NH_3 gas (Fig 3.28a). A black spot is formed due to metallic Ag and Mn(IV) oxide:



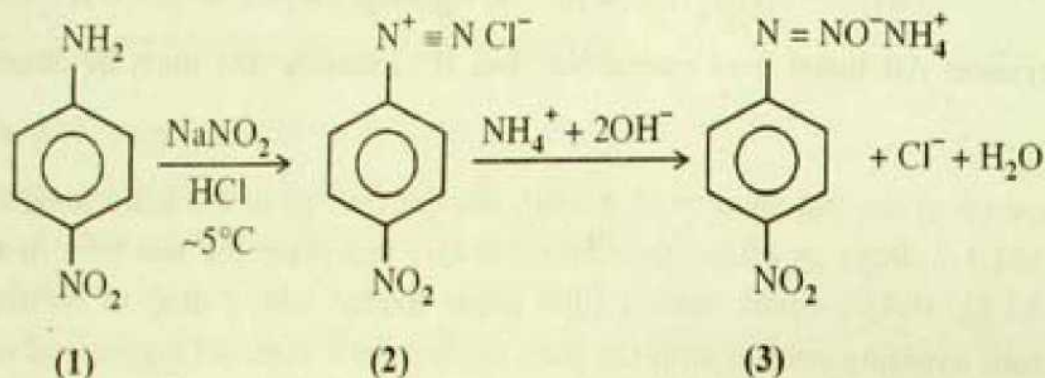
Limit of identification : 0.05γ of NH_3

Limit of dilution: 1 : 1×10^6

(5) *p*-Nitro benzenediazoniumchloride reagent

Reagent: Dissolve 1 g of *p*-nitroaniline ($p\text{-O}_2\text{N}-\text{C}_6\text{H}_4\text{-NH}_2$, 1) in 25 ml of 2M HCl and dilute to 160 ml with distilled water. Cool in an ice-bath to $\sim 5^\circ\text{C}$, add 20 ml of 5% NaNO_2 solution in water and shake until the precipitate dissolves. Keep in a cool and dark place (or in a dark coloured bottle). The reagent becomes turbid on keeping, but can be used after filtration.

Ammonium salts in presence of NaOH solution, react with *p*-nitrobenzenediazonium chloride (2) to produce a red colouration due to the NH_4^+ - salt (3) of the diazonium compound.



Place a drop of the neutral or slightly acidic test solution on a spot plate and add a granule of calcium oxide and then a drop of the reagent solution. A red zone appears around the calcium oxide. Run a blank test using a drop of water in place of the test solution.

Limit of identification: 0.7γ of NH_3 .

Limit of dilution : 1 : 7.5×10^4



CHAPTER - 5

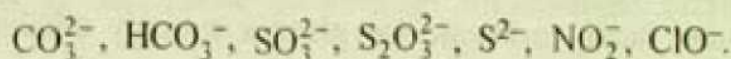
Reactions of Anion Radicals

5.1 Introduction

No systematic method has been developed for classification of the anion radicals into analytical groups like the cations. Anions may be broadly classified as *class A* and *class B* anions on the basis of their reactions with dilute hydrochloric or dilute sulfuric acid and concentrated sulfuric acid :

Class A anions : Decompose with evolution of gases, which are in most cases the anhydrides of the corresponding acids for the oxy anions and hydric acids or elemental gas molecules in case of halide and pseudo halide anions. Class A anions are again of two types :

(i) Decomposed by dilute hydrochloric or dilute sulfuric acid :

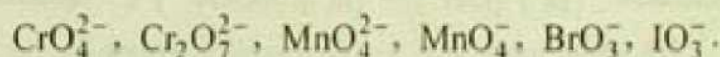


(ii) Decomposed by concentrated H_2SO_4 : All anions of type (i) and halides (F^- , Cl^- , Br^- , I^-), NO_3^- , BO_3^{3-} , SCN^- , BrO_3^- , $\text{Fe}(\text{CN})_6^{4-}$, $\text{Fe}(\text{CN})_6^{3-}$, MnO_4^- (**Danger**), ClO_3^- (**Danger**).

Class B anions : Characterised by reactions in solution involving precipitation and oxidation-reduction reactions:

(i) Precipitated by specific reagents : SO_4^{2-} , PO_4^{3-} , AsO_4^{3-} , AsO_3^{3-} , SiO_3^{2-} , CrO_4^{2-} ,

(ii) Oxidized or reduced occasionally involving colour change :



On the basis of their reactions in neutral solutions with zinc nitrate solutions, common anion radicals can be broadly classified into two groups :

(i) Those form precipitate with Zn^{2+} ,

(ii) Those do not form any precipitate with Zn^{2+} .

Such classification enables selective detection of anions in unknown materials (*cf.* Sect. 7.3). Reactions of individual anions leading to their indication, identification and confirmation will be discussed in this Chapter.

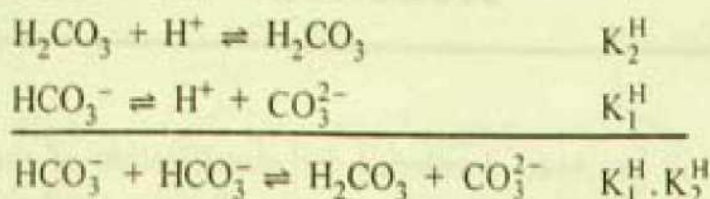
5.2 Reactions of Carbonate (CO_3^{2-}) and Bicarbonate (HCO_3^-)

Except the carbonates of alkali metals and ammonium carbonate, carbonates of most other metals are insoluble in water, but soluble in dilute mineral acids. Bicarbonates of most metals are soluble in water.

Carbonic acid (H_2CO_3) is a weak diprotic acid in aqueous solution,



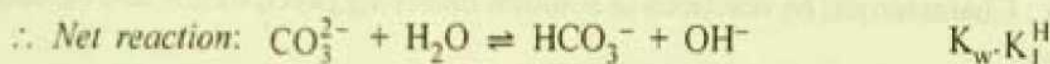
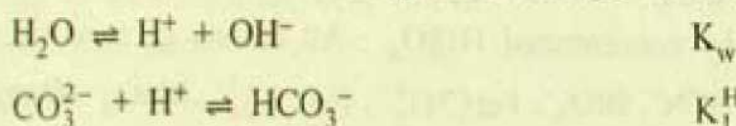
Carbonates and bicarbonates are extensively hydrolysed in aqueous solution. Bicarbonate ion being an *ampholyte*, forms a buffer solution of $pH \sim 8.34$, that is independent of its concentration.



$$K_1^H \cdot K_2^H = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} \times \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = [H^+]^2 \quad (\because [H_2CO_3] = [CO_3^{2-}])$$

$$\therefore pH = \frac{1}{2}(pK_2^H + pK_1^H) = \frac{1}{2}(6.35 + 10.33) = 8.34$$

Phenolphthalin indicator ($pK_m \sim 9.15$) solution remains in its colourless 'acid form' in bicarbonate. On the other hand, carbonate ion gives a strongly alkaline reaction in water.



$$\therefore [HCO_3^-] = [OH^-]$$

$$\therefore K_1^H \cdot K_w = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} \cdot [H^+][OH^-] = [H^+]^2 [CO_3^{2-}] \quad (\because [HCO_3^-] = [OH^-])$$

$$\therefore \frac{1}{[H^+]^2} = \frac{[CO_3^{2-}]}{K_1^H \cdot K_w}$$

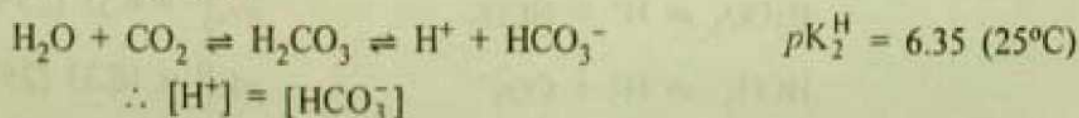
$$2pH = pK_1^H + pK_w + \log [CO_3^{2-}]$$

$$\therefore pH = \frac{1}{2}(pK_1^H + pK_w) + \frac{1}{2}\log [CO_3^{2-}].$$

$$\text{If } [CO_3^{2-}] = 1M, \quad pH = \frac{1}{2}(10.33 + 14.0) = 12.17 \text{ (strongly alkaline)}$$

$$\text{If } [CO_3^{2-}] = 0.1M, \quad pH = \frac{1}{2}(10.33 + 14.0) + \frac{1}{2}\log 0.1 = 11.67 \text{ (strongly alkaline)}$$

Thus, phenolphthalin indicator assumes its alkaline, red colour in a carbonate solution. Hence, it is possible to differentiate between carbonate and bicarbonate on the basis of their reactions with phenolphthalin indicator solution. Free carbonic acid (H_2CO_3) is not known, however, a saturated solution of CO_2 in water at 1 atm. pressure at room temperature is $\sim 0.03 M$, which is weakly acidic.



$$K_2^H = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = \frac{[H^+]^2}{[H_2CO_3]}$$

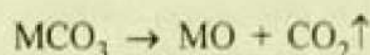
$$\therefore \frac{1}{[H^+]^2} = \frac{1}{K_2^H \cdot [H_2CO_3]}$$

$$\begin{aligned} \therefore pH &= \frac{1}{2} pK_2^H - \frac{1}{2} \log [H_2CO_3] \\ &= \frac{1}{2} \times 6.35 - \frac{1}{2} \log [0.03] = 3.94 \end{aligned}$$

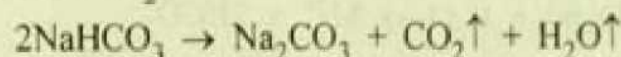
Indications

(1) Action of heat

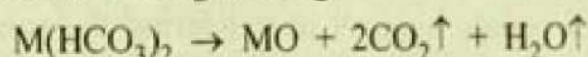
Alkali metal carbonates melt on strong heating. Carbonates of other metals decompose on strong heating.



Bicarbonates in general decompose on heating. Alkali metal bicarbonates on heating, produce carbonate and CO_2 .



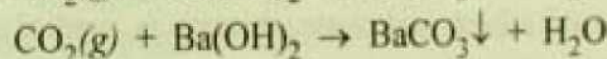
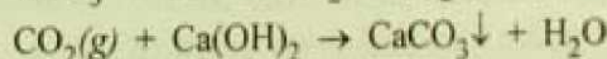
The residue (Na_2CO_3) on treatment with dil.HCl produces CO_2 . Other metal bicarbonates decompose to oxides on strong heating:



The residue (oxides, MO) does not produce CO_2 on treatment with dil.HCl.

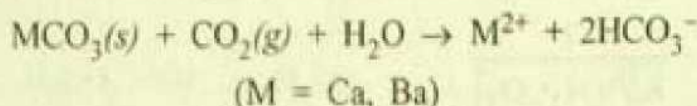
(2) Dilute hydrochloric acid

Both carbonate and bicarbonate decompose on treatment with dilute mineral acids (HCl, HNO_3 , H_2SO_4), evolving colourless, odourless CO_2 gas, which turns lime-water [$Ca(OH)_2$] and baryta-water [$Ba(OH)_2$] turbid due to precipitation of calcium and barium carbonates respectively.



Take a small amount ($\sim 0.2g$) of the solid sample in a semi-micro test tube fitted with a delivery tube with unequal arms, doubly bent at right angles. In another test tube take 1 ml of lime-water or baryta-water. Add 1 ml of dil.HCl in the sample tube and fix the delivery tube with the help of a cork in such a way that its shorter arm does not make contact with the reactants, whereas, the longer arm dips slightly into the lime (or baryta)-water solution (cf. Fig. 3.31). White precipitate of carbonates appear as soon as the CO_2 gas bubbles through the solution.

Continue passing the CO_2 gas. Gradually the white precipitate of carbonate disappears, due to the formation of bicarbonate, which is soluble in water :

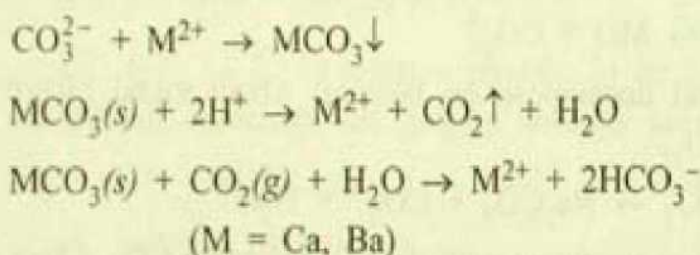


Reactions of Carbonate and Bicarbonate in solution

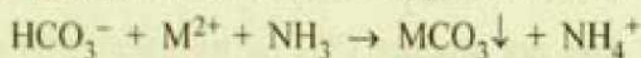
(1) Barium chloride (or Calcium chloride) solution

To a drop of the test solution in a semi-micro test tube add 1 drop of BaCl_2 (or CaCl_2) solution.

Carbonate : White precipitate of barium (or calcium) carbonate appears. The precipitate is soluble in dil. HCl , dil. acetic acid and also on passing CO_2 gas through the solution.



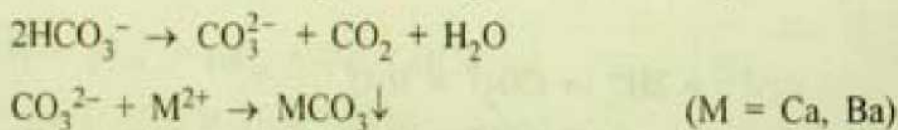
Bicarbonate : No precipitation with BaCl_2 or CaCl_2 solution in neutral or weakly acidic solution, but white precipitate of carbonate appears on rendering the solution ammoniacal.



(2) Boiling with water

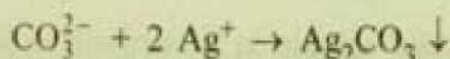
Carbonate : No change on boiling.

Bicarbonate : Decomposes to carbonate with evolution of CO_2 . White precipitate of carbonates appear on addition of BaCl_2 (or CaCl_2) to the resulting solution.

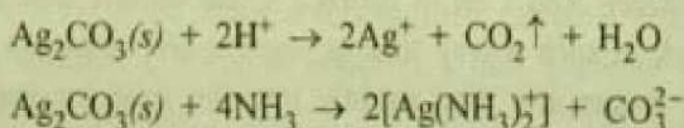


(3) Silver nitrate solution

Carbonate : White precipitate of silver carbonate appears in neutral solution.

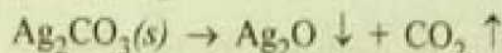


The precipitate is soluble in dil. HNO_3 and also in aq-NH_3 :

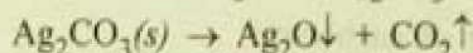
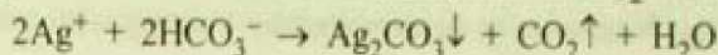


Caution : Discard the ammoniacal solution of $[\text{Ag}(\text{NH}_3)_2]^+$ complex to avoid explosion (cf. tests of silver and chloride p-236, 392).

On warming with excess reagent, silver carbonate decomposes to form brown coloured silver oxide with evolution of CO_2 ,



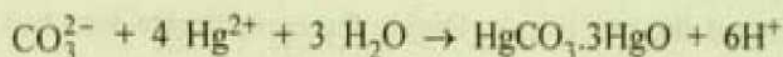
Bicarbonate : No precipitation in the cold on addition of AgNO_3 solution. But on boiling, bicarbonate decomposes with evolution of CO_2 with simultaneous precipitation of carbonate, which is ultimately transformed to brown precipitate of Ag_2O with evolution of CO_2 .



(4) Mercuric chloride (POISON)

Bicarbonate : No precipitation in the cold.

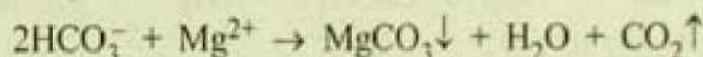
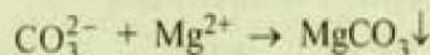
Carbonate : Brown precipitate of basic carbonate appears with release of protons, which react with unreacted carbonate to evolve CO_2 .



(5) Magnesium sulfate solution

Carbonate : White precipitate of MgCO_3 appears.

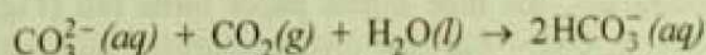
Bicarbonate : No precipitation in the cold, but on boiling, bicarbonate is transformed to carbonate and magnesium carbonate is precipitated with evolution of CO_2 ,



Confirmation

(1) Sodium carbonate-phenolphthalin reagent

Aqueous solution of sodium carbonate is strongly alkaline ($\text{pH} \sim 11-12$) due to hydrolysis of carbonate ion and phenolphthalin indicator ($\text{pK}_{\text{in}} \sim 9.2$) exists in its red coloured alkaline form in this solution. On the other hand, aqueous solution of bicarbonate ion is very weakly alkaline ($\text{pH} \sim 8.34$), in which phenolphthalin exists in its colourless acidic form. Therefore, when a red coloured solution of phenolphthalin in sodium carbonate is exposed to CO_2 , liberated from carbonate or bicarbonate on treatment of the latter with dilute mineral acid, the red colour is discharged, as carbonate is transformed to bicarbonate on reaction with CO_2 gas.



Place a small quantity (0.1 g) of the solid sample or 2-3 drops of concentrated aqueous extract of the sample in a semi-micro reaction tube and add a few drops of dil.HCl or H_2SO_4 . Fix an inverted dropper fitted with a rubber cork and containing a drop of red coloured sodium carbonate-phenolphthalin solution at the mouth of the test tube (Fig. 3.29b). The red colour disappears within a very short time. Run a blank test.

Anions which liberate acidic gaseous products on treatment with mineral acids, e.g. S^{2-} , $S_2O_3^{2-}$, SO_3^{2-} , NO_2^- and also F^- , CN^- , OCN^- etc. interfere. Reducing anions, e.g. S^{2-} , $S_2O_3^{2-}$, SO_3^{2-} , NO_2^- are rendered harmless by oxidizing the test solution with 4-5 drops of 10-volume H_2O_2 (3%) prior to acidification with H_2SO_4 (1M).

Adding a few drops of saturated $HgCl_2$ (POSITION) solution along with a few drops of dil.(1:4) H_2SO_4 , cyanides if present, are rendered innocuous, as mercuric cyanide that is formed, dissociates only very slightly. Nitrates may be removed by treating with aniline hydrochloride.

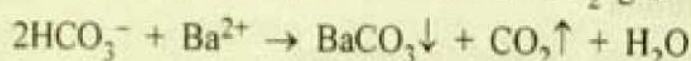
(2) Detection of bicarbonate in presence of carbonate

Take 1-2 drops of the test solution in a semi-micro centrifuge tube, add 1 drop of barium chloride solution. A white precipitate appears if carbonate is present. Add a few more drops of barium chloride until precipitation of carbonate is complete.

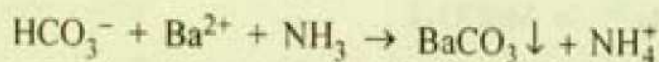
Note : This white precipitate may be due to carbonate, sulfate, sulfite, phosphate etc.

Centrifuge, and discard the precipitate. Divide the centrifugate into two parts. Perform the following two tests for bicarbonate.

2(a) Part-1 : Boil for some time. A white precipitate appears, as soluble bicarbonate is transformed to insoluble carbonate with evolution of CO_2 gas.



2(b) Part-2 : Add a few drops of *aq*- NH_3 until ammoniacal. White precipitate appears as HCO_3^- ion is transformed to CO_3^{2-} ion due to acid-base reaction with NH_3 ,



5.3 Reactions of Nitrite (NO_2^-)

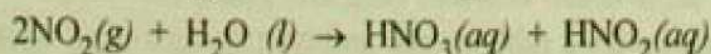
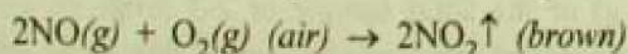
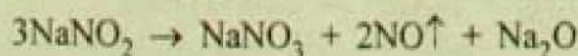
Solubility : Except silver nitrite, all nitrites salts are soluble in water. Aqueous solutions of nitrite salts are almost neutral or weakly alkaline to litmus (pK^H of $HNO_2 \sim 3.3-3.4$ at $25^\circ C$).

Indication

(1) Dry test tube heating

When a solid metallic nitrite salt is heated in a dry test tube, the nitrite decomposes and dark brown or reddish brown fumes of oxides of nitrogen are evolved.

(a) The issuing gas gives acidic reaction. If a blue litmus paper, moistened with a drop of water is held in the issuing gas, the blue litmus paper turns red (Fig. 3.29a).



(b) The issuing brown gas (NO_2) shows oxidizing reactions. If a starch iodide paper is

held in the issuing gas (Fig. 3.29a), the paper turns blue due to oxidation of iodide to iodine.



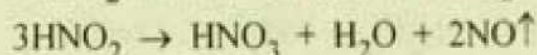
Limit of identification: 0.005g of HNO_2

Limit of dilution : 1 : 1×10^7

(2) Action of dil. HCl or dil. H_2SO_4

To a small quantity (0.1g) of the sample add 2 ml of dil. HCl or dil. H_2SO_4 (~2N) and warm gently.

A transient pale-blue colouration appears in the liquid (due to HNO_2) with evolution of brown fumes (due to NO_2) produced by combination of NO with O_2 of air.



(3) Conc. H_2SO_4 -Copper turnings

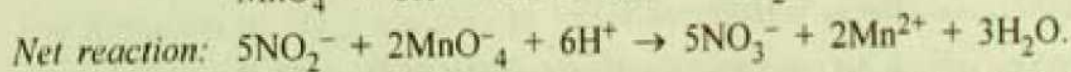
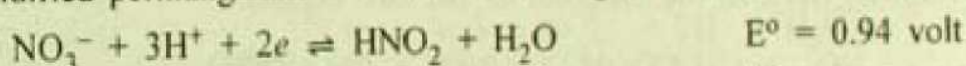
Perform this test inside a *Fume Cupboard*.

Take a small amount of (0.1g) of the solid sample in a dry test tube. Plug the mouth of the test tube with a piece of glass wool or asbestos fibre (Fig. 3.27a). Heat gently. Brown fume appears, which deepens on addition of a small amount of copper turnings.

Reactions of Nitrite ion in solution

(1) Oxidation to Nitrate

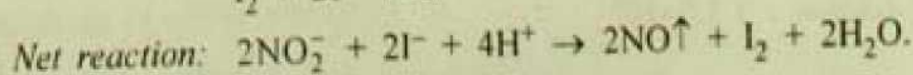
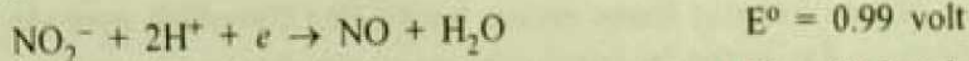
Strong oxidizing agent such as permanganate oxidizes nitrite to nitrate in acid medium. Pink colour of acidified permanganate solution is discharged on addition of nitrite solution.



Place 2-3 drops of the test solution on a spot plate, add 1 drop of 4N H_2SO_4 and 1 drop of very dilute potassium permanganate solution (N/100). Pink colour of KMnO_4 solution is at once discharged. [Dilute the permanganate solution if necessary].

(2) Reduction of Nitrite with evolution of NO or NH_3 gases

(a) In dilute acetic acid medium, nitrite oxidizes iodide to liberate iodine, and itself is reduced to NO gas.

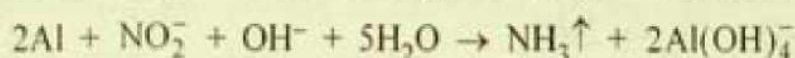
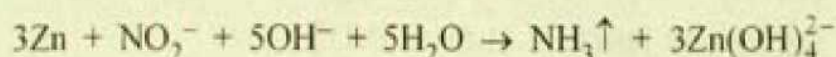


Liberated I_2 dissolves in excess iodide, forming brown coloured triiodide (I_3^-) complex ion. If this reaction is carried out in presence of starch indicator solution, a blue colouration is produced. The overall reaction in acetic acid medium is,



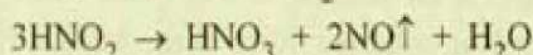
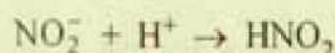
Place a drop of potassium iodide ($\sim 0.1N$) solution, 1 drop of starch indicator solution and 2 drops of dilute acetic acid ($\sim 2M$) in two adjacent cavities of a spot plate. Add 1 drop of the test solution in one of the cavities and one drop of distilled water to the other. An intense blue colouration is at once produced in the test solution. Compare with the blank.

(b) On boiling with Zn dust or Al metal or *Davarda's alloy* (Al 45%, Zn 5% and Cu 50%) in caustic alkali solution, nitrite is reduced to ammonia gas, which can be detected by its characteristic tests. (cf. NH_4^+ , Sect. 4.24) [Fig. 3.29 a,b].



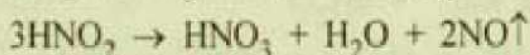
(c) Disproportionation of NO_2^- to NO_3^- and NO

Nitrite undergoes disproportionation to NO_3^- and NO in presence of dilute mineral acids.



(d) Brown ring test

If nitrite solution is slowly acidified with dilute acetic acid (or dilute H_2SO_4 or dilute HCl) in presence of freshly prepared ferrous sulfate ($FeSO_4$) or Mohr's salt, $((NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O)$ solution in dilute H_2SO_4 , nitric oxide (NO) produced from disproportionation of NO_2^- ion in presence of acid, forms a brown coloured complex, $[Fe(NO)(H_2O)_5]SO_4$, at the junction of the two liquids :



Coloured ions, iodide, bromide and other ions which produce coloured compounds with nitrite ion should be absent.

Take 1 ml of the test solution in a semi-micro test tube, add 1 ml of dilute ferrous sulfate solution, mix well, and cool under tap. Add very cautiously 1 ml of dilute acetic acid ($\sim 2M$) down the side of the inclined test tube. A brown ring is formed at the junction of the two liquids.

Note : Nitrate ion also forms similar brown ring for which conc. H_2SO_4 is to be used.

Limit of identification : 2% of HNO_2

Limit of dilution : $1:1.5 \times 10^6$

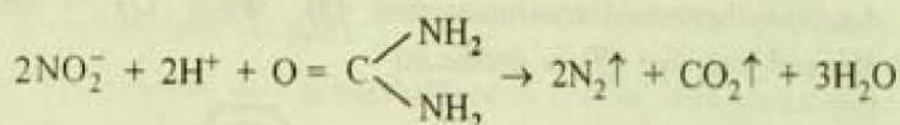
(3) Decomposition to nitrogen gas (Comproportionation reaction)

Nitrite ion undergoes comproportionation reaction with ammonium salts and amide derivatives such as urea, thiourea and sulfamic acid etc. In these reactions nitrite $N(3+)$ is reduced to elemental nitrogen $N(0)$ and amide $N(3-)$ is oxidized to elemental nitrogen $N(0)$ and N_2 gas is evolved.

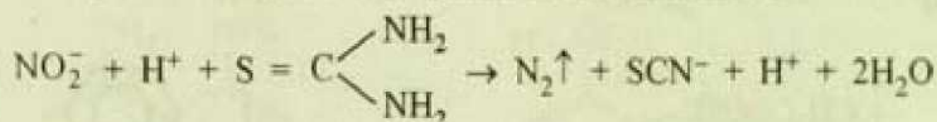
(a) When a nitrite salt solution is boiled with ammonium salt (NH_4Cl), effervescence of colourless odourless N_2 gas is evolved.



(b) On boiling a mixture of nitrite salt, urea and dil.HCl, nitrogen gas and carbon dioxide gas are evolved.

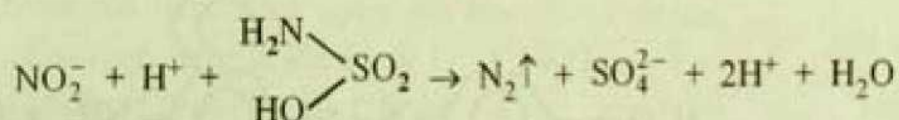


(c) When a mixture of nitrite salt, thiourea and dilute acetic acid is boiled, nitrogen gas is evolved and thiocyanate ion (SCN^-) is produced to the solution.



The presence of thiocyanate ion may be detected by treating the resulting solution with dil.HCl and $FeCl_3$ solution, when a blood red colouration due to $Fe(SCN)^{2+}$ complex ion is produced.

(d) When a nitrite salt solution is boiled with sulfamic acid, effervescence of N_2 gas is evolved and sulfate ion is produced in the solution.



The formation of SO_4^{2-} ion may be tested by treating the resulting solution with HCl and barium chloride solution, when a heavy white precipitate of $BaSO_4$ is produced.

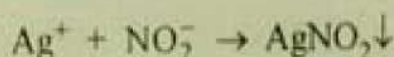
(e) Boiling with sodium azide (NaN_3) in presence of dilute H_2SO_4 also decomposes nitrite,



All these reactions 3(a-e) are useful in removing nitrite ion from a solution. Traces of nitrate (NO_3^-) ion may be produced in the reactions of NO_2^- with NH_4^+ salts, urea and thiourea, but not with the reaction with sulfamic acid or with sodium azide.

(4) Precipitation reaction with silver nitrate

Silver nitrate solution reacts with concentrated solution of nitrite salt to produce white precipitate of silver nitrite :



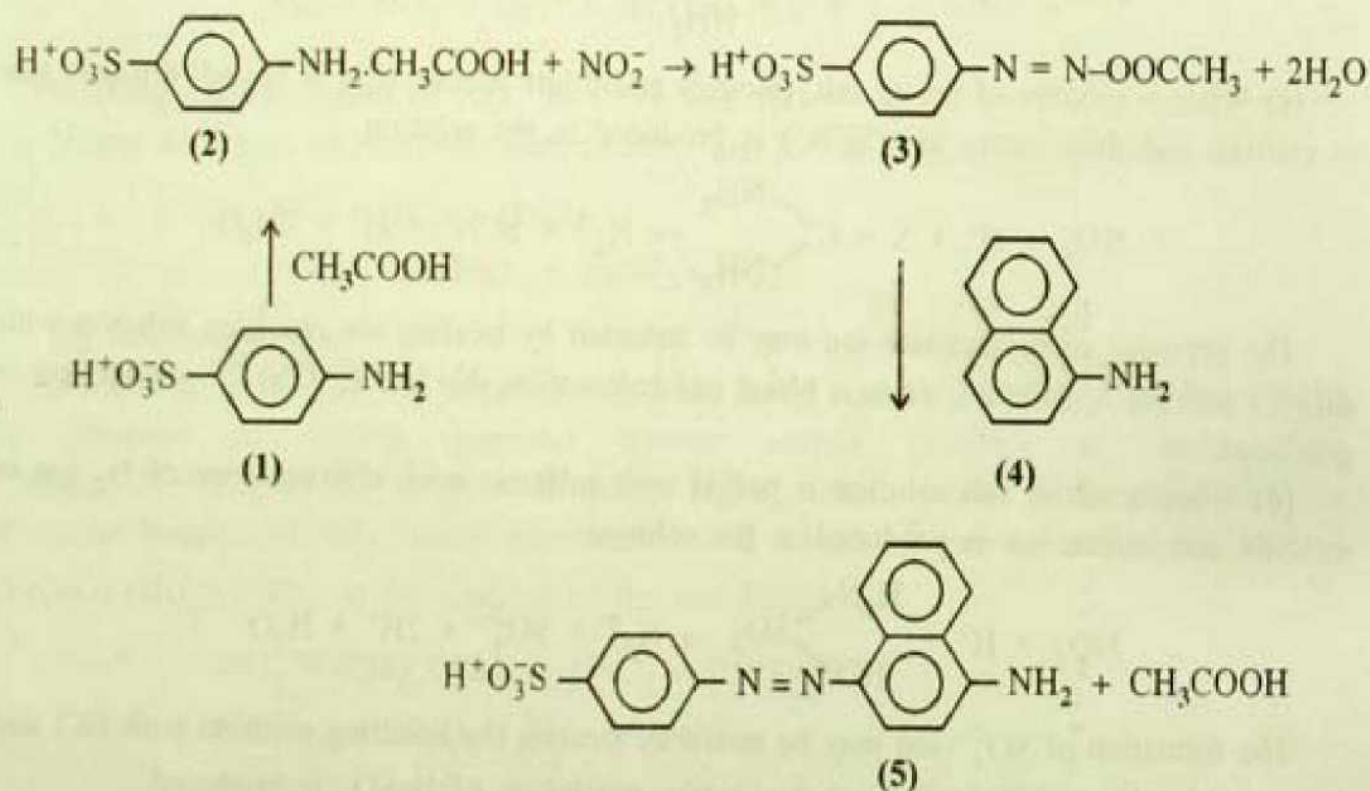
Confirmation

(1) Diazo-coupling reaction (Griess-Ilosvay test)

Reagents :

- (i) Sulfanilic acid : Dissolve 1g of sulfanilic acid (4-amino benzenesulfonic acid) in 30 ml of glacial acetic acid and dilute to 100 ml, cool to room temperature.
- (ii) 1-Naphthylamine : Boil ~ 0.3g of 1-naphthylamine with 70 ml of water, decant the clear solution from the blue violet residue, add 30 ml of glacial acetic acid and cool to room temperature. If the solution is coloured, add ~ 1g of zinc dust, stir for 3-4 minutes and filter, use the clear colourless filtrate.

In acetic acid solution, sulfanilic acid (1) exists as its acetate (2), which reacts with nitrite ion to produce 4-sulfonylbenzenediazoniumacetate (3). When (3) is coupled with 1-naphthylamine (4), the red azo dye (5) is produced.



Place a drop of the neutral or dilute acetic acid test solution on a spot plate add 1 drop of sulfanilic acid and mix well. Add 1 drop of 1-naphthylamine. A red colouration is produced if nitrite is present.

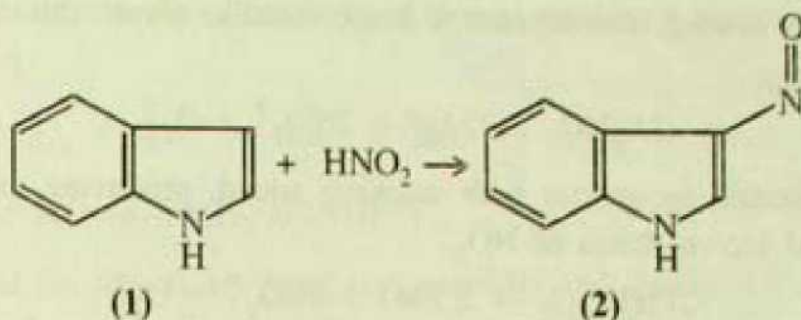
Limit of identification : 0.01γ of HNO_2

Limit of dilution : 1 : 5×10^6

(2) Indole reagent

Reagent : (0.015% solution in ethanol). Dissolve 15 mg of indole in 100 ml of 95% ethanol.

In dil. H_2SO_4 medium nitrous acid reacts with indole (1) to form purple-red coloured 3-nitroso indole (2).



Mix 1 drop of the test solution with ten drops of the indole reagent solution and 5 drops of dil. H_2SO_4 (~ 8M). A redish purple colouration is produced.

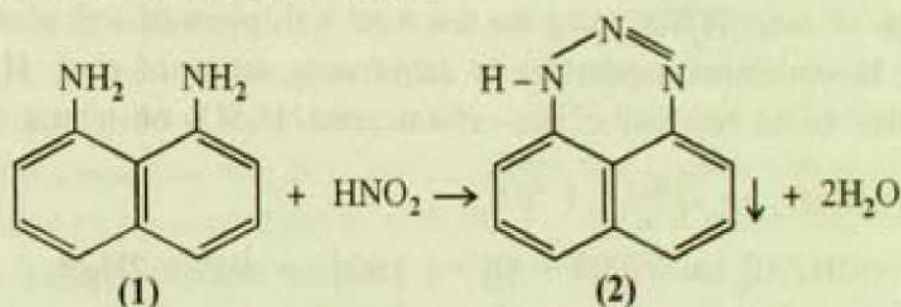
Limit of identification : 1γ of HNO_2

Limit of dilution : 1 : 1×10^6 .

(3) 1,8-Naphthalenediamine reagent

Reagent: 0.1% solution of 1,8-naphthalenediamine in 10% acetic acid.

In neutral solution nitrite ion reacts with 1,8-naphthalenediamine (1) to produce an orange-red precipitate of 1,8-aziminonaphthalene (2).



Mix a drop of neutral or dil.acetic acid test solution with a drop of the reagent in a semi-micro test tube and warm slightly on a hot water bath. An orange-red colouration or precipitate is produced depending upon the amount of nitrite.

Limit of identification : 0.1γ of HNO_2

Limit of dilution : 1 : 5×10^5 .

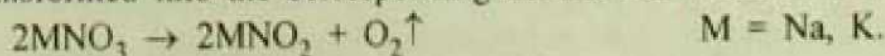
5.4 Reaction of Nitrate (NO_3^-)

All nitrate salts are soluble in water. Basic nitrates of bismuth (III) and mercury (II) precipitate on treatment with water, but dissolve in dilute mineral acids.

Indication

(1) Heating in dry test tube (in FUME CUPBOARD)

All nitrates decompose on heating, but, through different reactions. Alkali metal (Na, K) nitrates are transformed into the corresponding nitrites with evolution of O_2 gas.

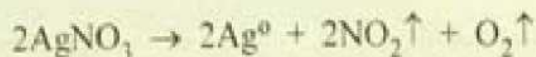


Ammonium nitrate decomposes to nitrous oxide through comproportionation reaction (cf. Sect 2.4).



N-oxidation states : (-3)(+5) (+1)

Silver nitrate, on heating, decomposes to black metallic silver with evolution of O_2 and brown fumes of NO_2 .



Heavy metal nitrates decompose with cracking sound, producing metallic oxides with evolution of O_2 and brown fumes of NO_2 .

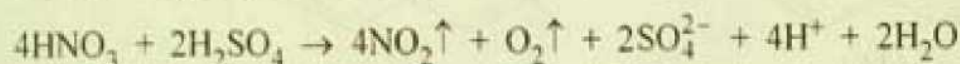


The brown fume of NO_2 gas is (i) acidic to blue litmus paper and (ii) oxidizing to starch iodide paper.

Place a small amount ($<0.1g$) of $Pb(NO_3)_2$ in a dry test tube plugged with a piece of glass wool and heat (cf. Fig. 3.29a). Brown fumes appear as nitrate is present. Hold a moisten blue litmus paper to the issuing gas, the litmus paper turns red. Hold a starch iodide paper to the issuing gas, the paper turns blue.

(2) Hot conc. H_2SO_4 (in FUME CUPBOARD)

Take a small amount ($<0.1g$) of the solid sample in a dry test tube, moisten the sample with a few drops of conc. H_2SO_4 , plug the test tube with piece of soft glass wool and heat (cf. Fig. 3.27a). Brown fumes appear due to dehydrating action of conc. H_2SO_4 on volatile HNO_3 formed due to the reaction of non-volatile conc. H_2SO_4 on nitrate salts :

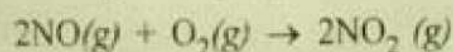
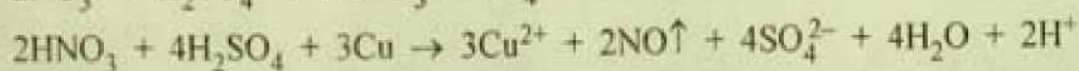


Dilute H_2SO_4 (or dil. HCl) has no effect on nitrate.

(3) Hot conc. H_2SO_4 + Cu-Turnings (in FUME CUPBOARD)

Perform the above test (2) adding a few pieces of clean copper turnings. Intense brown fumes appear due to NO_2 and a blue solution results due to Cu^{2+} ions.

HNO_3 formed from the reaction of nitrate salt with conc. H_2SO_4 , reacts with copper metal with evolution of NO gas, which on aerial oxidation produces intense brown coloured NO_2 gas.



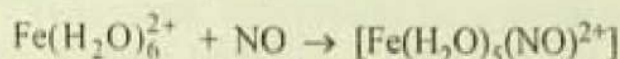
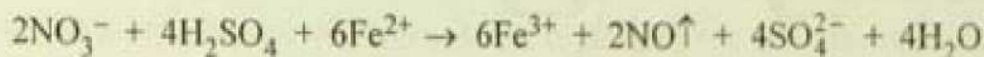
Test the acidic and oxidizing actions of NO_2 gas using (i) blue litmus paper and (ii) starch iodide paper (cf. Fig. 3.28 a,b; 3.29 a,b).

Reactions of Nitrate ion in solution

(1) Brown-ring test

In presence of conc. H_2SO_4 , nitrate is reduced to NO gas by $Fe(II)$ sulfate. The NO gas

thus produced, reacts with the unreacted Fe(II) sulfate to produce a brown coloured complex, $[\text{Fe}(\text{H}_2\text{O})_5(\text{NO})^{2+}]$ ion.



If the additions of the liquids are done very carefully and slowly, a brown coloured ring is formed at the junction of the two liquids.

(a) Place 1 ml of the test solution and 1-2 ml of conc. H_2SO_4 in a semi-micro test tube, mix well and cool under tap water. Add 1 ml of freshly prepared saturated ferrous sulfate solution (or Mohr's salt solution) down the side of the inclined test tube. A brown coloured ring is produced at the junction of the two liquids.

(b) Alternatively, take 1 ml of the test solution and 1 ml of freshly prepared ferrous sulfate (or Mohr's salt) solution in a test tube and mix well. Add ~ 1 ml of conc H_2SO_4 slowly down the side of the test tube. A brown ring is formed at the junction of the two liquids.

Metal ions such as Ba^{2+} , Sr^{2+} , Pb^{2+} , which form sparingly soluble sulfates, interfere by forming precipitate after addition of H_2SO_4 and ferrous sulfate. Bromide and iodide interfere, as free bromine and iodine impart colour to the test solution. The test is not also successful in presence of ferricyanide, ferrocyanide, chromate, sulfite, thiosulfate, thiocyanate and iodate. Interferences of the these ions may be eliminated if the test is done with the Na_2CO_3 extract of the sample, followed by neutralization with dil. H_2SO_4 and treatment with an excess of nitrate free silver sulfate solution, warming gently (~ 60°C) and then centrifuging off any precipitate. The brown ring test may be conducted in the clear centrifugate. Call this as the prepared solution for testing nitrate.

If nitrite is present, it interferes by imparting a brown colouration to the solution. Nitrite may be removed by boiling the centrifugate obtained after treatment with silver sulfate, with sulfamic acid, or urea or ammonium chloride or sodium azide (*cf. p-353*).

Place a large size crystal of ferrous sulfate or Mohr's salt on a spot plate, add a drop of the prepared solution for testing nitrate and a drop of conc. H_2SO_4 to run in at the sides of the drop. A brown coloured ring is formed round the crystal of Fe(II) sulfate if nitrate is present.

Limit of identification : 2.5γ of HNO_3

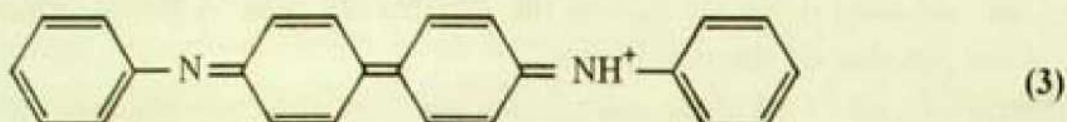
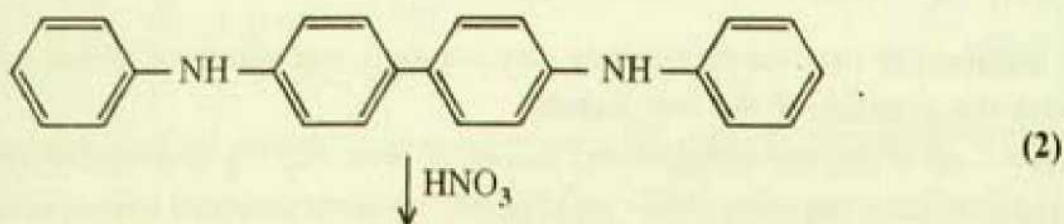
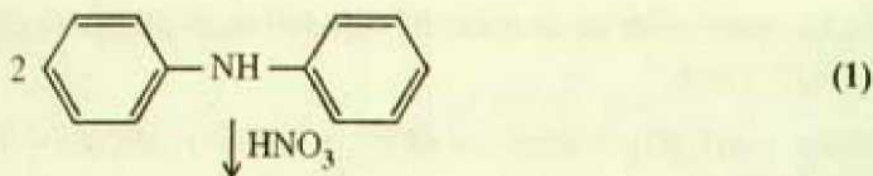
Limit of dilution : 1 : 2×10^4

(2) Diphenylamine or Diphenylbenzidine reagent : Blue ring test

Reagent : (0.5% solution in 80-85% H_2SO_4)

Take ~ 0.5g of diphenylamine or diphenylbenzidine in a beaker and cover the mass with conc. H_2SO_4 (~ 1-2 ml). Add water (15 ml) dropwise while stirring with a glass rod. After dissolution is complete, add more sulfuric acid (total 85 ml).

In conc. H_2SO_4 solution, nitrate (i.e. HNO_3) oxidizes diphenylamine (1), either through the colourless N,N'-diphenylbenzidine (2) or directly, to the blue-violet quinoid iminium ion (3).



Although the reaction is very sensitive, but it is not specific for nitrate, since many other oxidizing agents, viz. chromate, permanganate, bromate, iodate, chlorate, nitrite, higher valent metal oxides, peroxides, antimony (V), iron (III), (vanadate, molybdate, selenate)* also oxidize (1) through (2) to (3). Nitrite may be decomposed by treating with sodium azide.

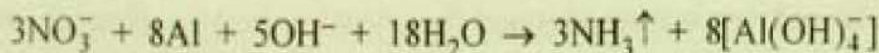
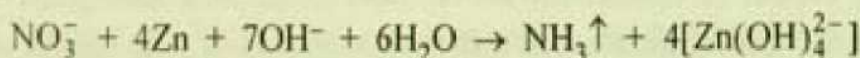
Take ~ 0.5 ml of the strongly acidic (H_2SO_4) solution of diphenylamine (1) or diphenylbenzidine (2) on a spot plate and place one drop of the test solution at the middle. A blue ring is formed as the two solutions mix. Intensity of the blue colour depends upon the quantity of nitrate.

Limit of identification : 0.5γ of HNO_3 with (1) and 0.07γ of HNO_3 with (2).

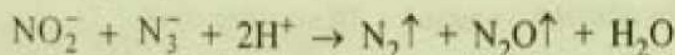
Limit of dilution : 1 : 1×10^5 with (1) and 1 : 7×10^5 with (2).

(3) Reduction to Ammonia

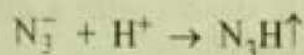
When boiled with zinc, aluminium or *Davarda's alloy* (Al, 45%, Zn, 5% and Cu, 50%) in presence of caustic alkali, nitrate is reduced to ammonia, which can be detected by its usual tests (*cf.* p.342).



Nitrite gives similar reactions and must be removed by boiling with sodium azide (NaN_3) in presence of dil. H_2SO_4 prior to treatment with (Zn/Al) and alkali.



Excess azide should be decomposed by boiling the acidic solution gently when hydrazoic acid, N_3H , volatilizes,



Note : For reduction of NO_3^- to NH_3 by metal-alkali mixture, removal of nitrite, if any,

*Rare elements

should be done by boiling the acidic test solution with sodium azide, but not with urea, or ammonium chloride or sulfamic and or thiourea, since unreacted parts of these materials may react with alkali to produce NH_3 gas. More over, removal of these unreacted materials is also difficult. Thiocyanate, ferrocyanide, ferricyanide and ammonium salts, which liberate ammonia under the condition of reduction of NO_3^- to NH_3 should be absent, or if present, these should be removed. These may be eliminated if the test for nitrate is done with the Na_2CO_3 extract of the sample followed by acidification with $\text{dil. H}_2\text{SO}_4$ and treatment with an excess of nitrate free Ag_2SO_4 solution as described before (*cf.* brown-ring test *p.*-357).

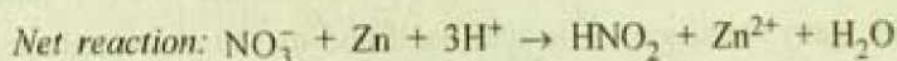
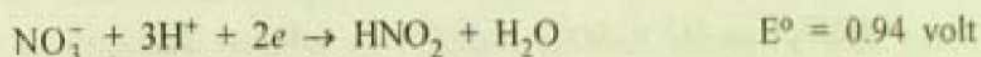
Ammonia liberated due to reduction of nitrate should be detected with phenolphthalin indicator paper, not with mercurous nitrate paper nor with Nessler's reagent paper nor with AgNO_3 - MnSO_4 reagent paper. Since arsenate, arsenite if present, are reduced to form arsine (AsH_3) gas, which blackens these reagent papers and spoil the detection of ammonia.

Confirmation

(1) **Brown ring test** in neutralized (by $\text{dil. H}_2\text{SO}_4$) Na_2CO_3 extract (described before).

(2) **Diazo-coupling test** after reduction to nitrite.

Nitrate is reduced to nitrite by zinc in dilute acetic acid medium,



The resulting nitrous acid (i.e., NO_2^-) may be detected by diazo coupling test with sulfanilic acid and 1-naphthylamine reagents as described under nitrite. If nitrite is present in the original sample, it has to be removed by any one of the methods described earlier.

Place a drop of the neutral or acetic acid test solution or a small quantity of the solid sample, on a spot plate, add 1 drop of sulfanilic acid mix well. Add 1 drop of 1-naphthylamine.

Two cases may arise :

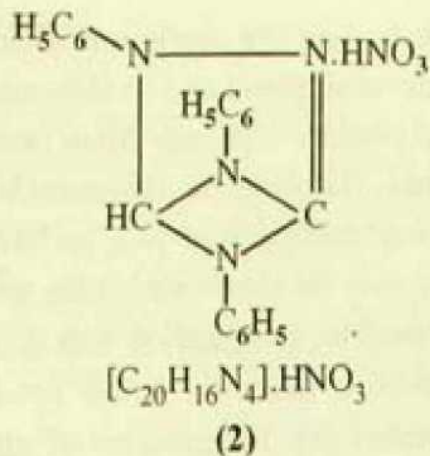
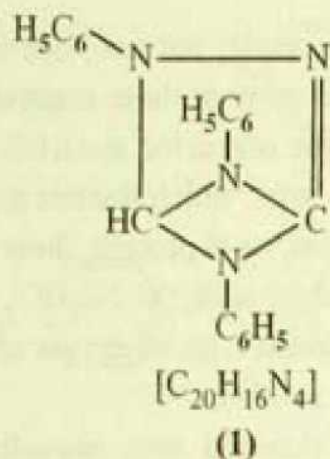
Case-I : A red colouration is not formed, so nitrite is absent. Add a small amount of zinc dust and stir with a glass rod. A red colouration develops. **Nitrate is present.**

Case-II : A red colouration is formed, **nitrite is present.** Remove nitrite from the test solution by any one of the methods described before (*cf.* *p.*-353) until the resulting solution does not give red colouration with sulfanilic acid and 1-naphthyl amine. Then add small amount of Zn dust and stir with a glass rod. If a red colouration develops at this stage, **nitrate and nitrite both are present in the sample.**

(3) **Nitron (diphenyl-endo-anilo-dihydrotriazole) reagent**

Reagent : 5% solution of nitron in 2(M) acetic acid.

Nitron base (1) reacts with acidic solution of nitrate to form sparingly soluble crystalline precipitate of nitron nitrate (2).



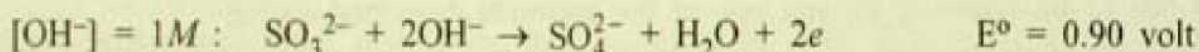
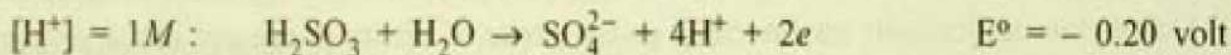
Bromide, iodide, nitrite, chromate, thiocyanate etc. also yield insoluble precipitates with this reagent and should be absent.

5.5 Reactions of Sulfite (SO_3^{2-}), Bisulfite (HSO_3^-)

Sulfurous acid (H_2SO_3) is known in solution only. It is a diprotic acid due to the ionization equilibria :



Consequently it forms two types of salts, viz. bisulfite (HSO_3^-) and sulfite (SO_3^{2-}). Salts of both these types are formed by many metal ions. The acid itself and its salts have reducing properties :



Naturally, sulfite and bisulfite salts are formed by metal ions not having redox properties. Alkali metal and ammonium salts are soluble in water. All other metal sulfites are sparingly soluble in water, but soluble in dilute mineral acids.

As the pK^{H} values imply, aqueous solutions of bisulfite salts are weakly acidic, whereas those of sulfite salts are alkaline to litmus due to hydrolysis of SO_3^{2-} ion,



Indication

(1) Dilute HCl (or Dilute H_2SO_4) [test in *FUME CUPBOARD*]

Sulfite and bisulfite salts decompose with liberation of SO_2 gas. The reaction is accelerated on warming,



SO₂ gas may be detected from its reducing and acidic properties.

To a small amount (~ 0.1g) of the solid sample (or its solution in water) in a test tube, add a few drops of dil. HCl (or dil.H₂SO₄), plug the test tube with a piece of cotton wool and warm slightly. If a colourless gas is evolved, (**CAUTION** : Suffocating, don't inhale), perform the following tests.

(i) Hold a filter paper moistened with acidified K₂Cr₂O₇ solution to the issuing gas (*cf.* Fig. 3.28 a,b; 3.29 a). The orange colour of K₂Cr₂O₇ is discharged and a green colour due to Cr³⁺(aq) ion appears, resulting from reduction of Cr₂O₇²⁻ by SO₂ (i.e., SO₃²⁻ ion) :



(ii) Hold a moistened starch-iodine paper to the issuing gas (*cf.* Fig. 3.29a). Blue colour of starch-iodine paper is discharged, as I₂ is reduced to I⁻ by SO₂ gas,

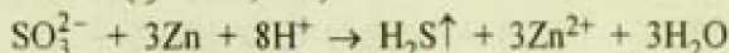


(iii) Hold a moistened blue litmus paper to the issuing gas (Fig. 3.28a). The blue litmus turns red, as SO₂ gives acidic reaction :



(2) Reduction by (Zn + dil.H₂SO₄)

Sulfite and bisulfite are reduced to sulfide (H₂S) on treatment with metallic Zn and dil.H₂SO₄ [**CAUTION** H₂S: smell of rotten eggs, poisonous, don't inhale]. H₂S may be detected by its characteristic tests (*cf.* Sect, 5.7)



Mix a small amount (0.1g) of the solid sample with small amount (~ 0.5g) of Zn dust in a test tube, plug the mouth of the test tube with a piece of cotton wool and add 1 ml of dil.H₂SO₄. Test the issuing gas as follows:

(i) Hold a drop reaction paper spotted with lead acetate solution. A black spot due to PbS is formed (*cf.* Fig. 3.27a),



(ii) Hold a drop reaction paper spotted with silver nitrate solution. A black spot due to Ag₂S is formed (*cf.* Fig. 3.28a),

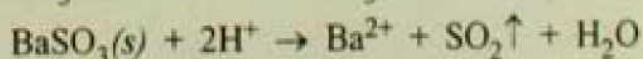
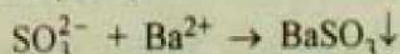


Reactions of Sulfite/Bisulfite ions in Solution and in Solid State

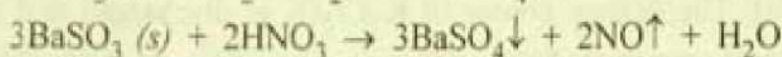
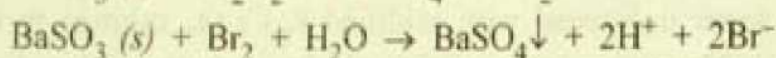
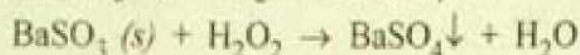
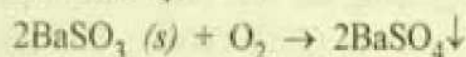
If the sample is not soluble in water, use the Na₂CO₃ extract of the sample after neutralization.

(1) Barium chloride solution

To 1 ml of the neutral test solution add 1 drop of BaCl₂ solution. White precipitate of BaSO₃ appears. The precipitate is soluble in dil. HCl with evolution of SO₂ gas.



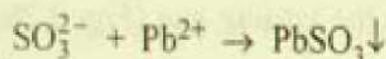
Precipitated BaSO_3 , on standing, is slowly oxidized by O_2 of the air to BaSO_4 which is not soluble in mineral acids. BaSO_3 , on warming with H_2O_2 , or Br_2 -water or conc. HNO_3 , is rapidly oxidized to BaSO_4 .



Dissolve the precipitate of BaSO_3 in dil. HCl and add a few drops of H_2O_2 or Br_2 -water, warm slightly. A heavy white precipitate of BaSO_4 comes down.

(2) Lead acetate solution

To 1 drop of the test solution in a semi-micro test tube, add 1 drop of lead acetate solution. White precipitate of PbSO_3 appears.



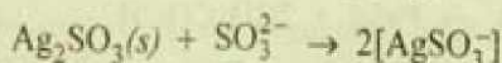
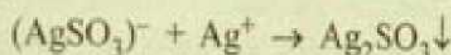
The precipitate is soluble in dil. HNO_3 . The precipitate is oxidized to lead sulfate by O_2 of air on boiling.



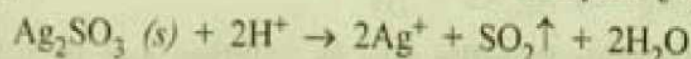
PbSO_4 is not soluble in dil. HNO_3 , but soluble in ammonium acetate on boiling (distinction from lead thiosulfate, which on boiling is transformed to black precipitate of PbS).

(3) Silver nitrate solution

When a dilute solution of silver nitrate is added to a sulfite solution, initially no visible change is observed, as the sulfitoargentate complex, $[\text{AgSO}_3^-]$ ion, that is formed, remains in solution. On addition of an excess of AgNO_3 solution, white crystalline precipitate of Ag_2SO_3 is formed, which passes into solution if more sulfite salt is added :

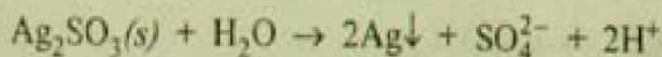


Precipitated Ag_2SO_3 is soluble in dil. HNO_3 with evolution of SO_2 . The precipitate is also soluble in *aq*- NH_3 solution due to the formation of complex $[\text{Ag}(\text{NH}_3)_2]^+$ ion.



Caution : Discard the ammoniacal solution of Ag_2SO_3 immediately to avoid explosion.

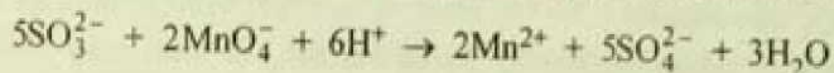
Precipitated Ag_2SO_3 on boiling with water, undergoes intramolecular redox reaction. SO_3^{2-} ion reduces Ag^+ ion to finely divided black metallic Ag and itself is oxidized to SO_4^{2-} ion.





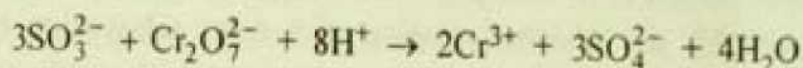
(4) Potassium permanganate-dil.H₂SO₄

To 1 ml of the test solution, add drops of dil. H₂SO₄ (not HCl) (~ 5N) until acidic. Add 1 ml of the acid in excess followed by 1 drop of very dilute KMnO₄ solution. Purple colour of permanganate solution is discharged. The change is rapid if the solution is slightly warmed.



(5) Potassium dichromate-dil.H₂SO₄

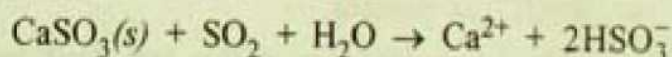
To 1 ml of the test solution Cr³⁺(aq) add drops of dil. H₂SO₄ (~ 5N) until acidic. Add 1 ml of the acid in excess and then add 1-2 drops of dilute K₂Cr₂O₇ solution. The orange colour of Cr₂O₇²⁻ ion is transformed into a green colour of Cr³⁺(aq), resulting from reduction of Cr₂O₇²⁻ ions by sulfite ion.



(6) Lime-water

Take a small amount (~ 0.2g) of the solid sample in a semi-micro test tube fitted with a double bent delivery tube, fitted with the test tube through a cork (*cf.* Fig. 3.31). Open the cork and introduce 1 ml of dil. H₂SO₄. Close the cork tightly and warm the contents gently. Pass the issuing gas through lime-water solution contained in another test tube.

A white precipitate of calcium sulfite is first formed, which passes into solution on prolonged passing of the SO₂ gas through it, due to transformation of sulfite into bisulfite ion,



Confirmation

(1) Sodium nitroprusside solution: Na₂[Fe(CN)₅NO].2H₂O

Reagents :

- (i) Mix ~ 0.1g of sodium nitroprusside and ~ 1 ml of water with a glass rod on a clean spot plate. Use this freshly prepared solution using a capillary dropper.
- (ii) Potassium ferrocyanide : ~ 1% solution in water.
- (iii) Zinc sulfate (or Zinc nitrate) : 0.25-0.5 (M) solution in water.

(a) Test for SO₃²⁻ or HSO₃⁻ in solution

SO₃²⁻ ion and SO₂ react with sodium nitroprusside giving a pale red colour, which is appreciably deepened in presence of Zn²⁺ ion and forms a red precipitate if potassium ferrocyanide is added. Possibly, like sulfide (S²⁻) ion, SO₃²⁻ ion and sodium nitroprusside form a complex, [Fe(CN)₅ NOSO₃²⁻] ion, which is adsorbed by the precipitate of potassium zinc ferrocyanide, K₂Zn₃ [Fe(CN)₆]₂, that is formed when Zn²⁺ and potassium ferrocyanide are added to the solution to produce the deep red colour.

Take one drop of zinc sulfate (or nitrate) solution in a semi-micro test tube, add one drop of 1% potassium ferrocyanide solution and then a drop of the sodium nitroprusside solution. White precipitate of potassium zinc ferrocyanide ($K_2Zn_3[Fe(CN)_6]_2$) appears. Now add a drop of the neutral test solution (or neutralized Na_2CO_3 extract). The colour of the precipitate becomes red if SO_3^{2-} is present.

Limit of identification : 3.2γ of Na_2SO_3

Limit of dilution : 1 : 16000

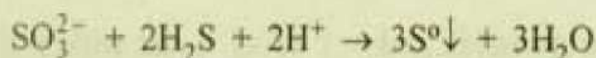
(b) Detection of sulfite/bisulfite by evolution of SO_2

Reagent : Zinc nitroprusside : To 1 ml of the sodium nitroprusside solution, add an excess of zinc sulfate (or nitrate) and boil for a few minutes. Wash the resulting precipitate with water by repeated centrifugation. Preserve the precipitate in dark.

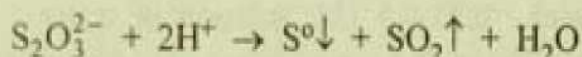
In contact with SO_2 gas, the salmon pink coloured zinc nitroprusside ($Zn[Fe(CN)_5NO]$) turns red coloured, possibly due to the formation of a weak adsorption compound between the two reactants. If the reaction product is held over ammonia, the colour of the unused zinc nitroprusside is discharged and the red colour of the reaction product becomes more prominent. Nitroprussides of metals other than zinc (eg. Cd^{2+}) also behave similarly.

Take a small amount ($< 0.1g$) of the solid sample or 1-2 drops of the test solution in a semi-micro reaction tube (Fig. 3.29 a,b). Hang a small amount of zinc nitroprusside slurry in the glass capillary (Fig. 3.29b) or impregnate a filter paper strip with zinc nitroprusside slurry (cf. Fig. 3.29a). Add 1 ml of 2N HCl in the reaction tube and then fix the cork at its mouth immediately. After the SO_2 gas has reacted with the reagent, remove the reagent slurry or reagent paper and hold the same over an open bottle of conc. ammonia for 1-2 minutes. The reagent is coloured deep red if SO_3^{2-} or HSO_3^{2-} is present.

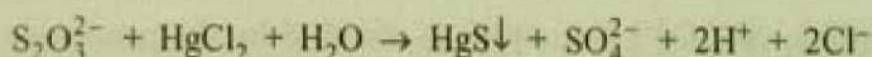
Sulfide (S^{2-}) and thiosulfate ($S_2O_3^{2-}$) ions interfere in this test. Sulfide on treatment with dil. HCl, liberates H_2S gas, which, apart from its reaction with alkaline nitroprusside solution, forming violet colouration, also reacts with SO_3^{2-} to precipitate elemental sulfur in milky colloidal form.



Thiosulfate itself decomposes on acidification, with precipitation of sulfur and liberation of SO_2 gas,



Sulfide and thiosulfate ions are to be removed before carrying out the nitroprusside tests for sulfite. Both these ions may be removed by treating the test solution with mercuric chloride, which reacts with S^{2-} and $S_2O_3^{2-}$ to form acid stable precipitate of black HgS.



$HgCl_2$ does not interfere with the liberation of SO_2 from sulfites/bisulfites on treatment with dil. HCl.

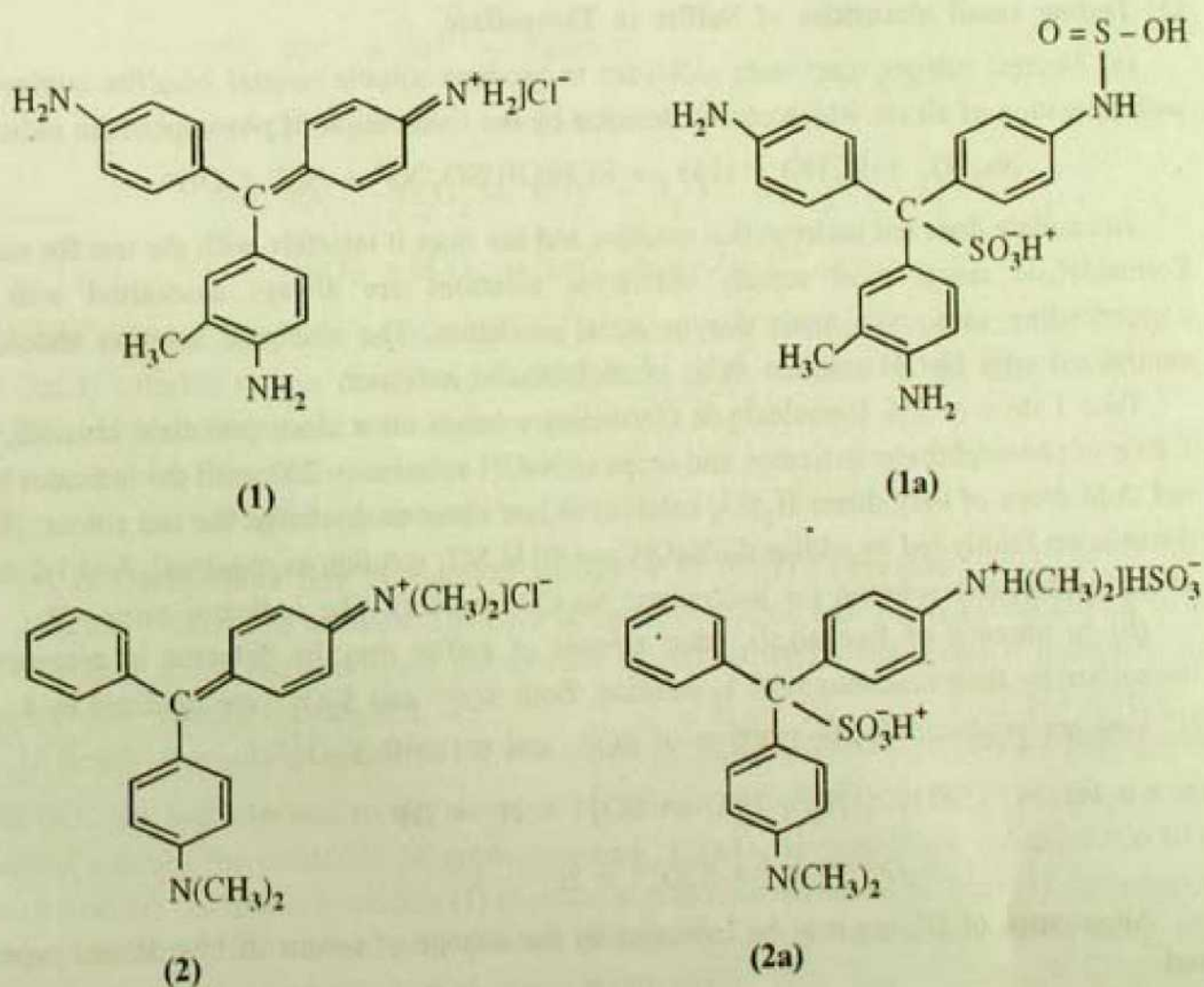
Place 1 drop of the test solution (i.e. neutralized Na_2CO_3 extract) in a semi-micro reaction tube (Fig. 3.29 a,b) add 2 drops of saturated mercuric chloride solution, stir with a glass rod. After 1-2 minutes, acidify the mixture with dil. HCl or dil. H_2SO_4 ($\sim 2N$) and immediately fix the glass dropper with its capillary filled with a slurry of zinc nitroprusside at the mouth of the reaction tube or hang a filter paper strip impregnated with zinc nitroprusside slurry (Fig. 3.29a). Wait for some time until the liberated SO_2 gas reacts with the reagent. Remove the reagent dropper or the reagent paper and expose it to ammonia gas for 1-2 minutes. A deep red colouration is produced if sulfite/bisulfite is present.

Limit of identification : 3.5 γ of SO_2

Limit of dilution : 1 : 14,000

(2) Fuchsin (or Magenta) test

Neutral solution of sulfite decolourises the aqueous solutions of triphenylmethane dyes, eg. fuchsin (1), malachite green (2), due to transformation of the quinoidal structures of these dyes to benzenoidal structures. Fuchsin (1) is transformed to the colourless N-sulfinic acid of *p*-fuchsin-luco-sulfonic acid (1a) and malachite green (2) into an addition compound (2a) with bisulfite ion.



The decolourised solution of fuchsin is known as *Schiff's reagent*. Aldehydes can restore the colour of Schiff's reagent.

Neutral solution of sulfite transforms the N-sulfinic acid of *p*-fuchsin leuco-sulfonic acid (1a) into its alkali salt. Decolourization is not complete with acidic solution of sulfites or sulfurous acid solution (SO₂-water). Acidic solutions of sulfites are to be neutralized with sodium bicarbonate, but not with Na₂CO₃ or NaOH, since free alkali interferes with the decolourization. If the sulfite solution is alkaline, it may be neutralized before hand with carbonic acid (in CO₂-water).

Thiosulfate, dithionate, polythionates do not interfere. Sulfide (S²⁻) and polysulfides (S_x²⁻) react similar to sulfite, and should be absent. Zn²⁺, Cd²⁺, Pb²⁺ interfere, so these are not suitable for removal of sulfide. These metal ions can not interfere, if the test is conducted with the neutralized Na₂CO₃ extract of the sample.

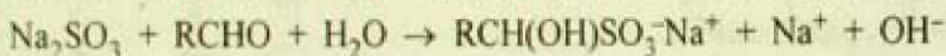
Place a drop of the dye stuff on a spot plate and add 1 drop of the neutral test solution (neutralized Na₂CO₃ extract). The dye is decolourized if sulfite is present.

Limit of identification : 1γ of SO₂

Limit of dilution : 1 : 5 × 10⁴

(3) Testing small quantities of Sulfite in Thiosulfate

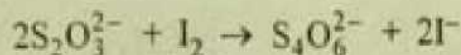
(a) Neutral sulfites react with aldehydes to produce soluble neutral bisulfite compounds with liberation of alkali, which can be detected by red colouration of phenolphthalin indicator.



Thiosulfate does not undergo this reaction and nor does it interfere with the test for sulfite. Formaldehyde reacts most rapidly. Aldehyde solutions are always associated with the corresponding carboxylic acids due to aerial oxidation. The aldehyde solution should be neutralized with NaOH solution using phenolphthalin indicator.

Take 1 drop of 1% formaldehyde (formalin) solution on a clean porcelain crucible, add 1 drop of phenolphthalin indicator, and drops of NaOH solution (~ 2N) until the indicator turns red. Add drops of very dilute H₂SO₄ solution to just about to discharge the red colour. [Keep the solution faintly red by adding dil. NaOH and dil. H₂SO₄ solution as required]. Add 1-2 drops of the neutral test solution (or neutralized Na₂CO₃ extract). The indicator turns red.

(b) In absence of free alkali, trace amount of sulfite may be detected in presence of thiosulfate by their reactions with I₂ solution. Both SO₃²⁻ and S₂O₃²⁻ are oxidized by I₂, but H⁺ ions are produced in the reaction of SO₃²⁻ and not with S₂O₃²⁻,



Appearance of H⁺ ion may be indicated by the change of colour of blue litmus paper to red.

Place 1 drop of the neutral test solution on a spot plate, add 1 drop of I₂ solution. Discharge



of brown colour of I_2 indicates the presence of reducing agents, such as SO_3^{2-} , $S_2O_3^{2-}$, S^{2-} etc. Add a few more drops of I_2 solution until the I_2 colour persists. Now place a strip of blue litmus paper in the brown solution, take out the paper immediately and then immerse the paper in 0.1N sodium thiosulfate solution to discharge the colour of I_2 adsorbed on it. The lower end of the paper is red coloured if sulfite is present.

Limit of identification : 5γ of Na_2SO_3 in presence of 1000 times

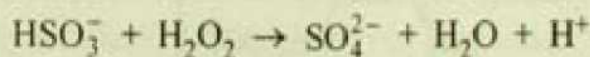
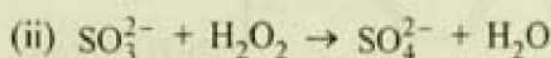
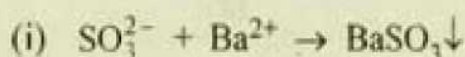
Limit of dilution : 1 : 10,000 the amount of $Na_2S_2O_3 \cdot 5H_2O$

(4) Distinction between Sulfites and Bisulfites

Reagents : (i) 1% $BaCl_2$ solution in water.

(ii) 3% H_2O_2 solution, shaken with $CaCO_3$ and filtered.

Soluble sulfites, due to hydrolysis give alkaline reactions in aqueous solution (discussed before), whereas, bisulfites are weakly acidic. Both sulfite and bisulfite (i) react with $BaCl_2$ to give white precipitate of barium sulfite and both are (ii) oxidized to sulfate by H_2O_2 . Reactions of both the reagents with bisulfite are accompanied by release of H^+ ion and the solution become, acidic, whereas, reactions of both the reagents with sulfite leave neutral solution.



Place 1 drop of the test solution on two adjacent cavities of a spot plate. Add 1 drop of the $BaCl_2$ solution to one cavity and 1 drop of the H_2O_2 solution to the other cavity. Test the two reaction mixtures with litmus paper.

Neutral reaction → Sulfite

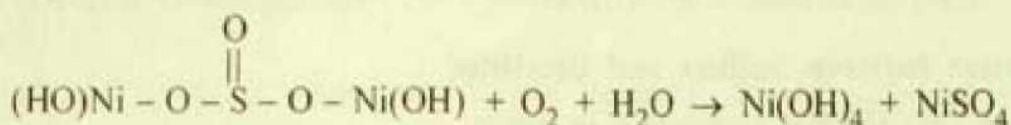
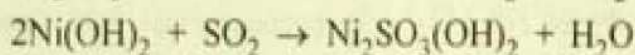
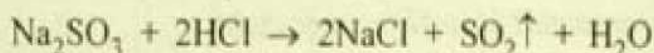
Acidic reaction → Bisulfite

(5) Benzidine-blue test by induced oxidation of Ni(II) hydroxide

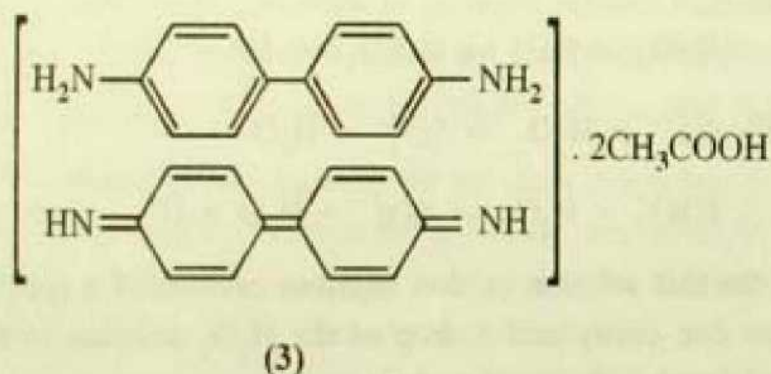
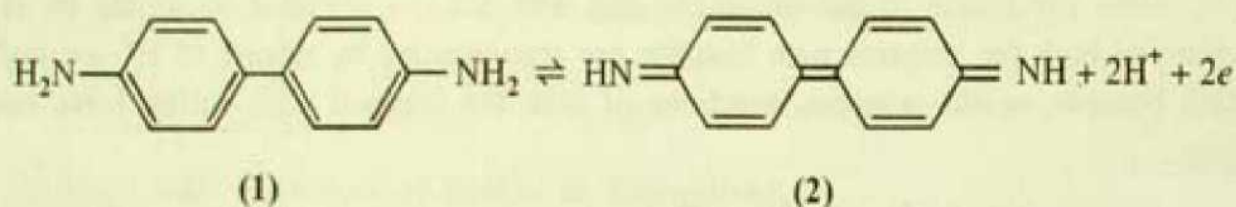
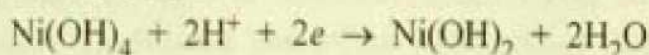
Reagent : Benzidine solution: Dissolve 0.05g of benzidine base or its hydrochloride in 10 ml of glacial acetic acid and dilute the solution to 100 ml with water. Filter if necessary and use the clear filtrate for the test.

If freshly precipitated alkali free green coloured Ni(II) hydroxide is brought into contact with SO_2 gas and exposed to air, autoxidation of SO_2 (i.e. SO_3^{2-}) to SO_4^{2-} occurs and this reaction induces the oxidation of green coloured $Ni(OH)_2$ to grey-black coloured $Ni(OH)_4$, which oxidizes colourless benzidine (1) in acetic acid medium to benzidine blue (3), that consists of the diamine (1) and its oxidation product diimine (2) in 1 : 1 molar proportion along with two equivalents of a monobasic acid (here, acetic acid).

SO₂ produced from the action of dilute hydrochloric (or sulfuric) acid on sulfite salts, reacts with Ni(OH)₂, and transforms it into basic Ni(II) sulfite, NiSO₃, Ni(OH)₂ or Ni₂SO₃(OH)₂, which is subsequently oxidized by oxygen of the air both cationically and anionically to produce Ni(IV) hydroxide, Ni(OH)₄ and Ni(II) sulfate :



Ni(OH)₄ oxidizes benzidine (1) to benzidine blue (3) in acetic acid medium and itself is reduced to Ni(II) state.



Strong oxidizing agents (viz, dichromate, nitrate, permanganate, peroxodisulfate, free halogens etc.), oxidize both sulfite and benzidine, and must be absent. Sulfide interferes by precipitating black NiS in neutral medium. More over SO₂ is used up by the H₂S generated from the reaction of sulfide with dilute acids :



So, sulfides, if present, must be removed before applying this test. Sulfide may be removed by precipitating as bismuth sulfide (Bi₂S₃) by treating the test solution with drops of bismuth nitrate solution in very dilute (1 : 20) hydrochloric acid medium, in which Bi₂S₃ is completely precipitated and may be removed by centrifugation. The test may even be applied in presence of the precipitate of bismuth sulfide, since the concentration of the acid is so low that it is without effect on Bi₂S₃.

Take a few drops of the test solution (or a small amount ~ 0.1g) of the solid sample in a semi-micro test tube in which a strip of filter paper impregnated with freshly precipitated

alkali free Ni(OH)_2 is hung with the aid of a platinum wire loop (Fig. 3.28a). Add $\sim 1 \text{ ml}$ of dilute ($2M$) HCl (or H_2SO_4), place a piece of clean cotton wool in the test tube to avoid spattering by bumping. Close the test tube with the cork from which the platinum wire loop containing the reagent $[\text{Ni(OH)}_2]$ paper is hung. Heat the test tube gently. The green colour of Ni(OH)_2 changes to grey black if sulfite is present. Take the reagent paper out and treat it with a drop of acetic acid solution of benzidine. A blue colouration indicates sulfite.

Limit of identification : 0.4γ of SO_2

Limit of dilution : $1 : 1.25 \times 10^5$.

5.6. Reactions of Thiosulfate ($\text{S}_2\text{O}_3^{2-}$)

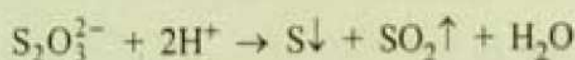
Barring sparingly soluble thiosulfates of lead, silver and barium, thiosulfates of most other metals are soluble in water. Thiosulfates of many metals dissolve in excess of sodium thiosulfate, forming thiosulfato complexes.

Indication

(1) Dilute Hydrochloric acid or Dilute Sulfuric acid

(a) To a small quantity ($\sim 0.1\text{g}$) of the solid sample, in a test tube (Fig. 3.29) add 1 ml of dil. HCl or dil. H_2SO_4 . Colourless gas with smell of burning sulfur (**Caution** : SO_2 gas is suffocating, do not inhale) is evolved. Hold an acidified dichromate paper or a drop of acidified dichromate solution to the issuing gas. The paper or the solution turns green if thiosulfate or sulfite or both are present.

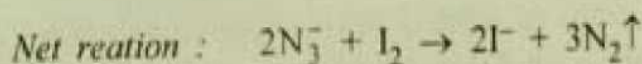
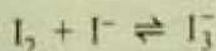
(b) To 1 ml of the test solution, add a few drops of dil. HCl (or H_2SO_4) as in the test 1(a). White turbidity appears along with evolution of colourless gas with smell of burning sulfur (distinction from sulfite) (**Caution** : SO_2 is poisonous). Hold an acidified dichromate paper or a solution at the issuing gas (Fig. 3.29). The paper or the solution turns green.



(2) Catalysis of Iodine-Azide reaction

Reagent : Dissolve 3g of sodium azide (NaN_3) in 100 ml of $0.1N$ I_2 solution in KI .

I_2 dissolves in KI to form the brown coloured tri-iodide (I_3^-) complex ion. Sodium azide does not react with I_2 or I_3^- . But in presence of thiosulfate, sulfide and thiocyanate the brown colour of I_2 (or I_3^-) is discharged at once with evolution of a colourless and odourless neutral (to litmus) gas i.e. N_2 gas.



Take 1-2 drops of brown coloured solution of I_2 in KI on a spot plate and add 1 drop of the test solution or a small amount of the solid sample. Stir with a glass rod. If the brown

colour of I_2 (or I_3^-) is at once discharged with effervescence of N_2 gas, the sample contains thiosulfate and or sulfide and or thiocyanate.

Limit of identification : 0.15% of $Na_2S_2O_3 \cdot 5H_2O$

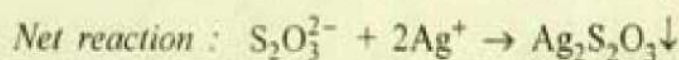
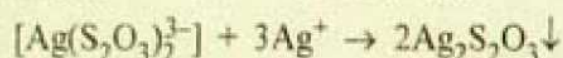
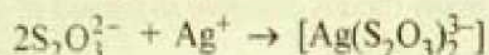
Limit of dilution : 1 : 3.3×10^5 .

Reactions Thiosulfate ion in solution

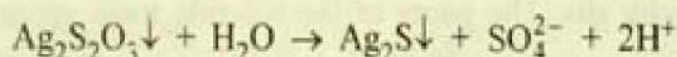
Use the aqueous extract or a neutralized Na_2CO_3 extract.

(1) Silver nitrate solution

On addition of small amount of $AgNO_3$ solution to a large excess of thiosulfate solution, no precipitate is formed due to the formation of dithiosulfato argentate (I) complex $[Ag(S_2O_3)_2]^{3-}$ ion. On addition of more $AgNO_3$, white precipitate of silver thiosulfate, $Ag_2S_2O_3$, appears :

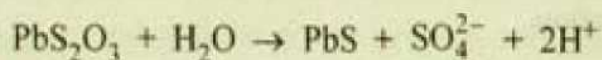
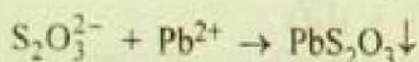


Precipitated $Ag_2S_2O_3$ is an unstable compound. On standing, the precipitate of $Ag_2S_2O_3$ changes colour from white, through yellow, brown to black Ag_2S due to disproportionation of $S_2O_3^{2-}$ ion. The transformation is accelerated on warming.



(2) Lead acetate solution

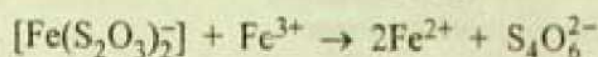
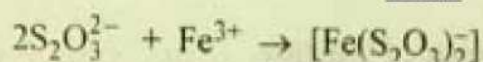
When lead acetate is added to a thiosulfate solution, white precipitate of lead thiosulfate is formed, which is soluble in excess of thiosulfate solution due to complex formation. The white precipitate of lead thiosulfate on boiling, is gradually transformed to black precipitate of PbS .



(3) Ferric chloride solution

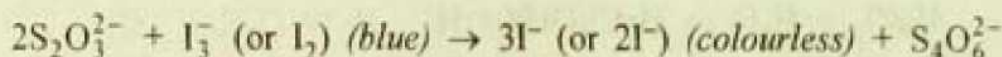
Reagent: Neutral ferric chloride solution: Aqueous solution of ferric chloride is acidic due to hydrolysis of $Fe^{3+}(aq)$ ion (cf. Set. 2.1). To prevent precipitation of $Fe(OH)_3$, ferric chloride solution is made in dilute hydrochloric acid. Take 1 ml of ferric chloride solution in a test tube add drops of dilute (1 : 4) $aq-NH_3$ solution with shaking until a redish brown colour persists in the solution, but brown precipitate of $Fe(OH)_3$ is not formed. Centrifuge if necessary and use the clear centrifugate for the tests.

To 1 ml of the neutral test solution add 1-2 drops of neutral ferric chloride solution. A deep violet colouration appears due to the formation of dithiosulfato iron (III) complex. On standing, the violet colour gradually disappears as $Fe(III)$ oxidizes $S_2O_3^{2-}$ ion to tetrathionate ($S_4O_6^{2-}$) ion and itself is reduced to $Fe(II)$.



(4) Iodine (or Potassium tri-iodide, KI_3) - Starch solution

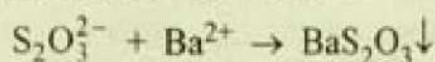
Thiosulfate is oxidized to tetrathionate ($\text{S}_4\text{O}_6^{2-}$) ion by I_2 (or KI_3), the latter is reduced to iodide. If the reaction is carried out in presence of starch indicator solution, which forms an intense blue coloured adsorption compound with I_2 (or I_3^-), the blue colour is at once discharged.



This reaction forms the basis of iodometric titrations. Sulfide and sulfite also discharge the iodine colour, and should be absent.

(5) Barium chloride solution

To 1-2 drops moderately concentrated test solution in a semi-micro test tube, add 1 drop of barium chloride solution and scratch the sides of the test tube with a glass rod. White precipitate of barium thiosulfate appears.



(6) Blue ring test

Thiosulfate reduces molybdate to *molybdenum blue* (cf. Sect. 8.8). Mix 1 ml of the test solution with equal volume of ammonium molybdate solution and pour the mixture down the side of another test tube containing 1 ml of conc. H_2SO_4 . A blue ring is temporarily formed at the junction of the two liquids.

Confirmation

(1) *Tris*-ethylenediamine Nickel (II) nitrate (or chloride)

$[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ (or Cl_2) reagent

Reagent : To 2 ml of 0.5 M nickel (II) nitrate (or chloride) add ethylenediamine [$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$, i.e., en] until a violet colour appears. Use this freshly prepared reagent for testing thiosulfate.

When a neutral solution of thiosulfate is added to a freshly prepared solution of $[\text{Ni}(\text{en})_3](\text{NO}_3)_2$ or $[\text{Ni}(\text{en})_3]\text{Cl}_2$, a crystalline violet precipitate of thiosulfate salt of the complex is formed.



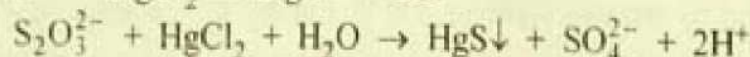
Sulfide, sulfate, tetrathionate, thiocyanate do not interfere. But H_2S and $(\text{NH}_4)_2\text{S}$ decompose the reagent by precipitating black NiS . With modification, the test may also be applied to detect Ni^{2+} in presence of Cu^{2+} , Co^{2+} , Fe^{2+} and Cr^{3+} .

Limit of dilution : 1 : 2.5×10^4

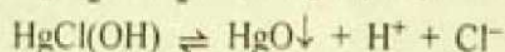
(2) Test for Thiosulfate in the presence of Sulfide

Reagent : 2% mercuric chloride solution in water.

(a) HgCl_2 reacts with both sulfide and thiosulfate to form black precipitate of mercuric sulfide (HgS), but the reaction with thiosulfate solution is accompanied by release of H^+ , which may be detected from the change of colour of blue litmus to red.



Mercuric chloride in aqueous solution may be slightly acidic due to hydrolysis, and this may mislead the identification,



This problem may be overcome by adding some potassium chloride, which forms soluble complexes, $\text{K}[\text{HgCl}_3]$ and $\text{K}_2[\text{HgCl}_4]$ with HgCl_2 and prevents its hydrolysis.

Place a drop of 2% mercuric chloride solution and a small crystal of KCl on a spot plate, mix with a glass rod. Add 1-2 drops of the neutral test solution (or neutralized Na_2CO_3 extract). Black precipitate of HgS appears if thiosulfate, or sulfide or both are present. [A white precipitate of $\text{HgCl}_2 \cdot 2\text{HgS}$ may appear if an excess of HgCl_2 is present]. Now dip a blue litmus paper into the mixture. Two cases may arise :

- (i) black precipitate of HgS but no change of litmus colour from blue to red
→ sulfide is present.
- (ii) black precipitate of HgS with change of litmus colour from blue to red
→ thiosulfate is present.

If a black precipitate is not formed on addition of HgCl_2 , then both sulfide and thiosulfate are absent.

(b) To a few drops of the neutral solution of sulfide and thiosulfate on a spot plate, add a few small crystals of cadmium nitrate (or sulfate), mix with a glass rod. Sulfide is precipitated as yellow cadmium sulfide (CdS), but thiosulfate remains in solution. Now dip a strip (1 cm × 5 cm) of quantitative (Whatman No. 1) filter paper into the resulting suspension. The clear solution containing the thiosulfate ascends the filter paper, leaving at its lower end the yellow precipitate of CdS . Remove the paper after 2-3 minutes and cut the clear moist portion off the portion containing the CdS precipitate. Now cut the moist portion of the paper into two pieces, allow to dry and perform the following tests :

(i) Add a drop of 2% HgCl_2 solution containing little KCl , to the moist paper. A black spot (of HgS) is formed. Add 1-2 drops of water using a capillary tube, so that a moist portion spreads out of the black spot. Now add a drop of methyl red indicator on the moist portion. A red colouration appears if thiosulfate is present.

(ii) Dip the other portion of the cut filter paper into 1-2 drops of iodine-azide reagent taken on a spot plate. A perceptible evolution of bubbles of colourless odourless gas (N_2) with discharge of brown colour of I_2 -azide reagent occurs, if thiosulfate is present. Some bubbles are seen to adhere to the spot plate even if the paper is removed.

5.7 Reactions of Sulfide (S^{2-}), Hydrosulfide (HS^-)

Hydrogen sulfide (H_2S) is a weak diprotic acid (*cf.* Set. 2.1, 2.2) in water.

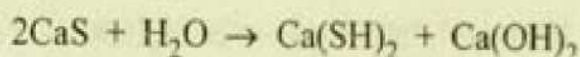


Consequently it forms two types of salts, normal sulfide (S^{2-}) and hydrosulfide (HS^-). Alkali metal and ammonium sulfides are soluble in water, and such solutions give alkaline reactions due to hydrolysis of sulfide and hydrosulfide ions.

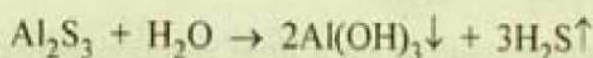


At ordinary temperature and 1 atm. pressure, H_2S dissolves in water, and the saturated solution of H_2S is $\sim 0.1M$ in $[H_2S]$ under this condition.

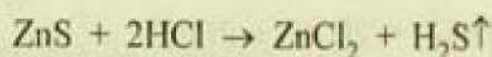
Sulfides of metals other than alkali metals are sparingly soluble in water. Transition metal sulfides and sulfides of metals around the right hand bottom of the modern periodic table are identifiable from their characteristic colours. Alkaline earth metal sulfides are hydrolysed to hydrosulfides and hydroxides,



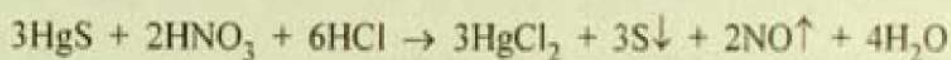
Sulfides of Al(III), Cr(III), and Mg(II) are completely hydrolysed to form hydroxides with evolution of H_2S :



Sulfides of Fe(II), Mn(II), Zn(II) and alkali metals are decomposed by dil. HCl with evolution of H_2S gas :

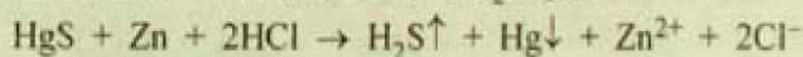


Pb(II), Cd(II), Ni(II), Co(II), Sb(III, V), Sn (IV) sulfides are decomposed by conc. HCl, not by dil. HCl. Mercuric sulfide is insoluble in even in conc. HCl, but soluble in aqua-regia with separation of elemental sulfur :



Acid insoluble sulfides (HgS , CdS , As_2S_3 etc.) are decomposed :

(i) by Zn/HCl or Sn/HCl with evolution of H_2S gas,



(ii) by fusion with anhydrous Na_2CO_3 followed by extraction of the fused mass with water.



Except these acid insoluble sulfides, the other sulfides pass into Na_2CO_3 extract in water.

Indication

(1) Dilute HCl (or Dil. H_2SO_4)

Except the sulfides of mercury, arsenic, cadmium and antimony, sulfides of all other metals,

or the Na_2CO_3 extract or the Na_2CO_3 fusion extract of the sample on treatment with dilute HCl (or dil. H_2SO_4) decompose to liberate colourless H_2S gas, having disagreeable odour (smell of rotten eggs) and detected by its characteristic tests.

(a) Take a small quantity ($\sim 0.1\text{g}$) of sample or 1 ml Na_2CO_3 extract or Na_2CO_3 fusion extract or the aqueous extract of the sample as required in a semi-micro test tube. Plug the test tube with a piece of pure cotton wool (*cf.* Fig. 3.27). Add $\sim 1\text{ ml}$ of dil. HCl or dil. H_2SO_4 . Warm gently and test the issuing gas as follows :

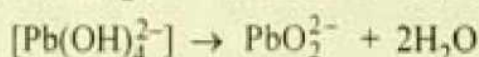
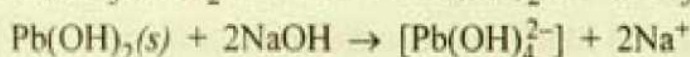
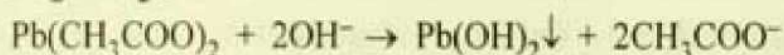
(i) Hold a filter paper moistened with lead acetate solution at the issuing gas. A black spot results due to PbS .



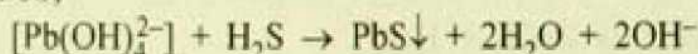
(ii) Hold a filter paper moistened with cadmium acetate (or any cadmium salt) solution at the issuing gas for ~ 2 minutes. A yellow spot results due to CdS . Hold the paper over ammonia for better colouration.

(iii) *Test with Plumbite solution $\text{Na}_2[\text{PbO}_2]$*

Place a drop of lead acetate solution on a spot plate add drops of dil. NaOH ($\sim 2M$) solution. A white precipitate of $\text{Pb}(\text{OH})_2$ that is initially formed, dissolves in excess alkali, forming sodium plumbite ($\text{Na}_2[\text{PbO}_2]$)



Now take one drop of the plumbite solution on a drop reaction paper using a capillary tube and hold the paper at the issuing gas (Fig. 3.27a). Immediate blackening occurs due to the formation of PbS ,

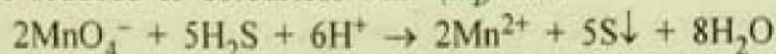


(b) Reactions of H_2S as a reducing agent

Fix a double bent glass tube with a cork at the mouth of the test tube (Fig. 3.31). Treat the test sample or the solution as in test 1(a) and pass the evolved gas through the following reagents.

(i) KMnO_4 solution acidified with dil. H_2SO_4 :

Purple colour of permanganate is discharged, as it oxidizes H_2S to precipitate elemental sulfur and itself is reduced to colourless $\text{Mn}^{2+}(\text{aq})$ ion.



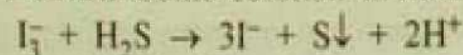
(ii) $\text{K}_2\text{Cr}_2\text{O}_7$ solution acidified with dil. H_2SO_4 or dil. HCl :

The orange colour of dichromate solution is transformed to green colour of $\text{Cr}^{3+}(\text{aq})$ ion with precipitation of sulfur, as $\text{Cr}_2\text{O}_7^{2-}$ oxidizes H_2S and itself is reduced to $\text{Cr}^{3+}(\text{aq})$ ion.



(iii) Starch-iodine (or starch I_3^-) reagent:

Blue colour of starch-iodine solution is discharged with precipitation of sulfur,



The solution becomes acidic due to release of H^+ ions. Blue litmus paper turns red if it is dipped into the resulting solution.

(2) Catalysis of iodine-azide reaction

Azide N_3^- ion does not react with I_2 (or I_3^-). In presence of trace amount of sulfide, thioulfate and thiocyanate, immediate discharge of iodine colour with effervescence of N_2 gas takes place as these anion radicals catalyse the reaction,



So this is a selective reaction for sulfide. It may be made specific for sulfide if thiosulfate and thiocyanate are removed.

Place a drop of sodium azide solution on two adjacent cavities of a spot plate and add 1 drop of iodine solution (0.1N) in each cavity. Now add 1 drop of the test solution or a small amount of the powdered sample in one of the cavities and an equal volume of water in the other cavity. Discharge of brown colour of iodine solution with effervescence from the former indicates sulfide and or thiosulfate and or thiocyanate.

(3) Silver nitrate solution

Place 1 drop of the test solution on a spot plate and add 1 drop of silver nitrate solution. Immediate blackening occurs due to precipitation of Ag_2S .



(4) Barium chloride-dil.HCl solution

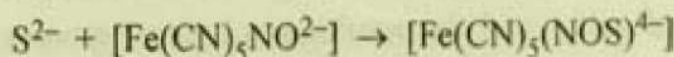
No precipitation occurs as the solubility product of BaS is much higher.

Confirmation

(1) Sodium nitroprusside solution

Reagent : Freshly prepared solution of 0.1g of $Na_2[Fe(CN)_5NO].2H_2O$ in ~ 1 ml of water.

Sulfide ion in alkaline or ammoniacal solution forms a violet colouration with sodium nitroprusside, possibly due to the formation of pentacyanonitrosylsulfide complex of iron, $[Fe(CN)_5(NOS)]^{4-}$ ion,



Mix a drop of the alkaline or ammoniacal test solution with 1 drop of sodium nitroprusside. A violet colouration appears if sulfide is present.

Alternatively, filter paper (Whatman No. 1) impregnated with the sodium nitroprusside reagent may be treated with a drop of the test solution. A violet spot results if sulfide is present.

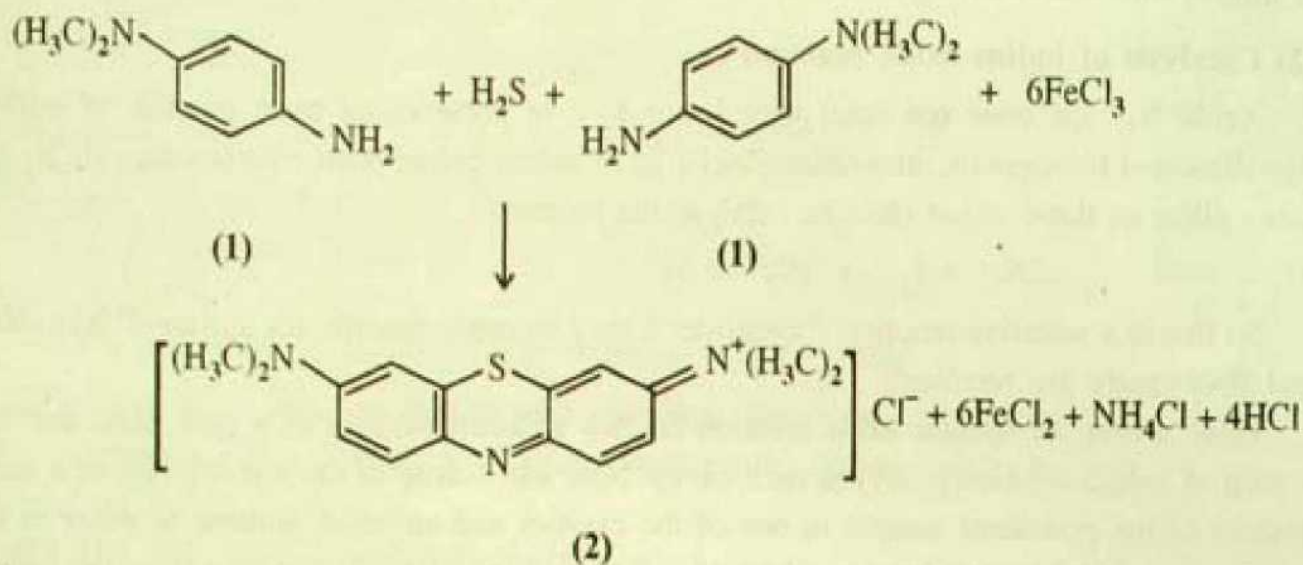
Limit of identification : 1γ of Na_2S

Limit of dilution : 1 : 5×10^4 .

(2) Methylene blue test

In the presence of ferric chloride, H_2S reacts with N,N-dimethyl-*p*-phenylenediamine

(1) to produce a blue coloured water soluble dye stuff, methylene blue (2) having quinoidal structure.



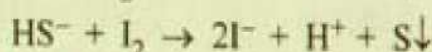
Mix one drop of the test solution, one drop of conc. HCl and a few grains of N, N-dimethyl-*p*-phenylenediamine (or 1 drop of its chloride or sulfate salt solution) on a spot plate. Then add 1 drop of 0.5 (M) ferric chloride solution in dil. HCl. An intense blue colouration is produced due to the formation of methylene blue.

Limit of identification : 1γ of H₂S

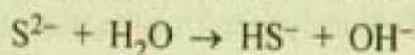
Limit of dilution : 1 : 5×10⁴.

(3) Test for hydrosulfide (SH⁻) in presence of sulfide (S²⁻)

Both sulfide (S²⁻) and hydrosulfide (SH⁻) are oxidized by iodine solution.



Aqueous solutions of alkali metal sulfides (e.g. Na₂S, K₂S) are strongly alkaline due to hydrolysis of sulfide ion and turn red litmus blue,



On reaction of the iodine solution with sulfide (S²⁻) ions, the brown colour of iodine is discharged with precipitation of sulfur and the resulting solution becomes neutral to litmus as S²⁻ ions disappears from solution. Hydrosulfide solutions are weakly alkaline, but on reaction with I₂ solution, sulfur is precipitated with release of H⁺ ions, for which the resulting solution becomes distinctly acidic and turns blue litmus paper red.

Take 1 drop of the test solution on a spot plate and add drops of 0.1N iodine solution. Sulfur is precipitated with discharge of iodine colour. Add a few more drops of iodine solution until some iodine colour persists in the solution. Add a drop of CS₂ and stir the mixture with a glass rod. Both precipitated sulfur and unreacted iodine dissolve in CS₂. Now dip a blue litmus paper into the aqueous part of the reaction mixture. The blue litmus turns red if hydrosulfide (HS⁻) is present.

5.8 Reactions of Thiocyanate (SCN^-)

Except alkali metal and the ammonium salts, thiocyanates of most other metals are sparingly soluble in water.

Indication

(1) Catalysis of iodine-azide reaction

Azide (N_3^-) does not react with iodine (I_2 or I_3^-). But thiocyanate is a powerful catalyst for the iodine-azide reaction,



This reaction is a selective test for thiocyanate, since sulfide and thiosulfate ions also catalyse this reaction.

Take 1 drop of I_2 solution (in KI, i.e. I_3^-) on two adjacent cavities of a spot plate, add a small crystal of sodium azide in both the cavities. Now add a small amount ($\sim 0.1\text{g}$) of the powdered solid sample, or its aqueous extract, or, Na_2CO_3 extract in one cavity and an equal volume of water in the other cavity. Stir with a glass rod.

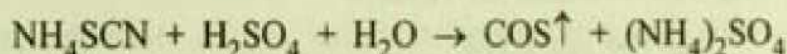
Brown colour of iodine is at once discharged with colourless and odourless effervescence of nitrogen gas, if thiocyanate and or thiosulfate and or sulfide are present.

Limit of identification : 1.5 γ of KSCN

Limit of dilution : 1 : 3.3×10^4 .

(2) Concentrated H_2SO_4 (To be conducted in FUME CUPBOARD)

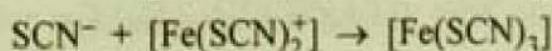
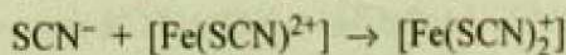
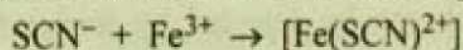
On warming with conc. H_2SO_4 , thiocyanates decompose to form carbonylsulfide, COS gas [Caution : Poisonous] along with sulfate ion. Carbonylsulfide burns with a blue flame if ignited [cf. Fig. 3.30a].



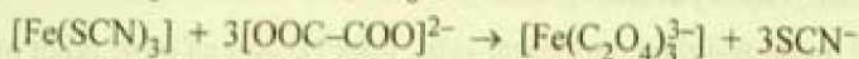
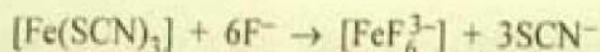
Note : The reaction is much more complex, since SO_2 and CO_2 are also detected in the gaseous product. The resulting solution also contains formic acid and sulfur. With dilute acid ($<3M$) no reaction occurs in the cold. A yellow solution is formed on boiling.

(3) Ferric chloride solution

In dilute acidic ($\sim 0.5M$) solution, thiocyanate ion reacts with Fe^{3+} ion to produce blood-red coloured complexes $[\text{Fe}(\text{SCN})^{2+}]$, $[\text{Fe}(\text{SCN})_2^+]$ etc.,



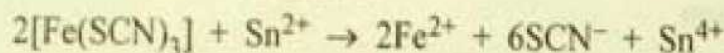
Iodide ion interferes, as Fe^{3+} oxidizes I^- to liberate I_2 , which forms brown colouration in the solution. Stability of $\text{Fe}^{\text{III}} - \text{SCN}^-$ complexes are not very high, as Fe^{3+} is a hard Lewis acid, whereas, SCN^- is a soft Lewis base. These complexes decompose on addition of harder Lewis base ligands, such as, fluoride, phosphate, oxalate, citrate, tartarate etc., with discharge of the blood red colour.



The blood-red colour is also discharged when soft Lewis acid metal ions, such as, $\text{Hg}(\text{II})$, $\text{Ag}(\text{I})$ -nitrates are added,



The blood-red colour is discharged if Fe^{III} is reduced to Fe^{II} by addition of a reducing agent, such as stannous chloride solution :

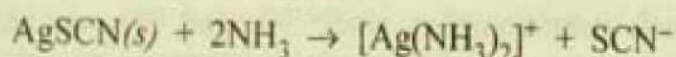


Place 1 drop of the weakly acidic test solution on four adjacent cavities of a spot plate, add one drop of dilute ferric chloride solution to each cavity. Blood-red colouration is produced in each cavity if SCN^- is present. Now perform the following tests :

- (i) Add a crystal of ammonium bifluoride in one of the cavities and stir with a glass rod. Blood red colour is discharged.
- (ii) Add a crystal of oxalic acid to another cavity and stir. Blood-red colour is discharged.
- (iii) Add 1 drop of mercuric chloride to the third cavity and stir. Blood red colour is discharged.
- (iv) Add 1 drop of stannous chloride in the fourth cavity and stir. Blood-red colour is discharged.

(4) Silver nitrate solution

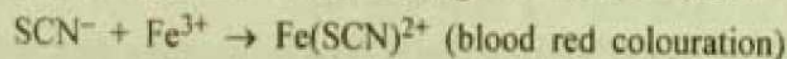
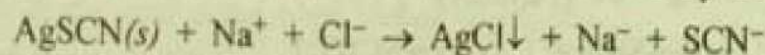
When silver nitrate solution is added to a neutral or weakly acidic (HNO_3) solution of thiocyanate, a curdy white precipitate of silver thiocyanate (AgSCN) appears. The precipitate of AgSCN , like AgCl and AgBr , is soluble in ammonia solution, due to the formation of the complex, $[\text{Ag}(\text{NH}_3)_2]^+$ ion, but insoluble in HNO_3 .



Caution : The ammoniacal solution containing $[\text{Ag}(\text{NH}_3)_2]^+$ should be discarded immediately after the test to avoid explosion.

Separation of Thiocyanate from Halides

Silver thiocyanate ($pK_{sp} \sim 11.92$), when digested with a concentrated ($\sim 1M$) solution of sodium chloride, undergoes metathesis reaction to form silver chloride ($pK_{sp} \sim 9.82$) setting free some thiocyanate ions in solution, which can be detected by ferric chloride test.



(5) Cobalt nitrate solution

In dilute acidic solution, thiocyanate reacts with Co^{2+} ion, producing blue colouration due of the formation of tetrathiocyanatocobaltate (II) complex, $[\text{Co}(\text{SCN})_4]^{2-}$ ion.



In a clean porcelain crucible, mix two drops of the test solution, one drop of cobalt nitrate solution (0.5 M) and evaporate the mixture to dryness by warming gently on a hot water bath. The residue will be violet coloured, whether thiocyanate is present or not. The violet colour slowly fades. Add a few drops of acetone and stir with a glass rod. A blue-green to green colouration is produced if thiocyanate is present.

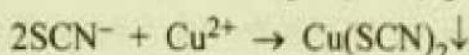
If nitrite is present, a red colour is produced due to the formation of nitrosyl thiocyanate (NOSCN). Nitrite should be removed by boiling with ammonium chloride (*cf. p-353*).

Limit of identification : 1% of SCN^-

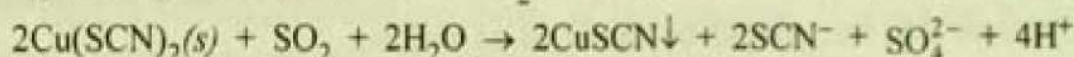
Limit of dilution : 1 : 5×10^4 .

(6) Copper sulfate solution

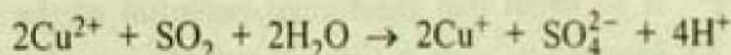
When Cu^{2+} ion reacts with thiocyanate ion, a green colouration is first produced possibly due to formation of complex ion of the type, $\text{Cu}(\text{SCN})^+$, and finally a dark green to black precipitate of $\text{Cu}(\text{SCN})_2$ is formed.



The black precipitate of $\text{Cu}(\text{SCN})_2$ is transformed to a white precipitate of cuprous thiocyanate (CuSCN) on treatment with SO_2 - water, which reduces Cu^{2+} to Cu^+ ,



If Cu^{2+} is first reduced with SO_2 -water and then treated with thiocyanate, white precipitate of CuSCN is directly formed :



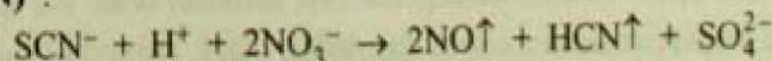
(a) Place 1 drop of dilute copper sulfate solution on a spot plate. Add 1-2 drops of the test solution. A transient green colouration appears, which is followed by a black precipitate. Now add 1 drop of dil. H_2SO_4 (~ 1N) and drops of SO_2 -water (or a crystal of sodium sulfite) and stir with a glass rod. The black precipitate gradually becomes white.

(b) Place a drop of copper sulfate solution on a spot plate, add 1 drop of dilute H_2SO_4 (~ 1N) and drops of SO_2 -water (or a crystal of sodium sulfite) until the blue colour of copper sulfate is discharged. Add a drop of the weakly acidic test solution. A white precipitate appears if thiocyanate is present.

CAUTION : The following reactions of thiocyanate produce poisonous gaseous products. These reactions should not be carried out in the open. May be done with great caution only under a FUME CUPBOARD with adequate exhaust arrangement.

(i) Reaction with dilute nitric acid

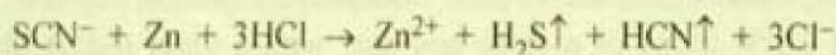
Thiocyanate decomposes on warming with HNO_3 , producing nitric oxide and hydrogen cyanide (POISON) :



With conc. HNO_3 , the reaction is vigorous and both CO_2 and NO gases are produced.

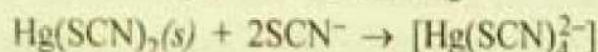
(ii) Zinc-dilute HCl

Poisonous HCN and H₂S gases are produced when thiocyanate reacts with Zn and dilute hydrochloric acid,



(iii) Mercuric nitrate solution (POISON)

A white precipitate of mercuric thiocyanate is formed when mercuric nitrate solution reacts with thiocyanate. The precipitate is soluble in excess of the thiocyanate solution due to the formation tetrathiocyanatomercurate (II) or mercuriothiocyanate, $\text{Hg}(\text{SCN})_4^{2-}$ complex ion.



CAUTION : Precipitated mercuric thiocyanate on heating, swells up enormously, forming a poisonous polymeric cyanogen derivative, known as '*Pharaoh's serpents*'.

Confirmation

(1) Ferric chloride test (*cf. p.-377*)

(a) Thiocyanate in presence of iodide

Iodide ion interferes in the test as Fe^{3+} oxidizes I^- to I_2 , which forms a brown colouration. If iodide is present this test should be modified as follows.

To 1 drop of very dilute ferric chloride solution on a spot plate, add 1-2 small crystals of ferrous sulfate (or Mohr's salt) and mix with a glass rod. In the resulting $\text{Fe}^{3+} - \text{Fe}^{2+}$ mixture, the proportion of $\text{Fe}^{3+} : \text{Fe}^{2+}$ is so small that the formal potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple ($E^0 = 0.77$ volt) is appreciably lowered to such a value that Fe^{3+} ion of this couple fails to oxidize iodide of the $\text{I}_2/2\text{I}^-$ couple ($E^0 = 0.53$ volt) but its concentration is sufficient to produce a recognisable blood red colouration with thiocyanate ion.

(a) Place 1 drop of very dilute FeCl_3 solution on a spot plate, add 1-2 crystals of ferrous sulfate (or Mohr's salt) and 1 drop of dil. HCl ($\sim 0.5M$), mix with a glass rod. Add a drop of this $\text{Fe}^{3+}/\text{Fe}^{2+}$ mixture on a drop reaction paper and allow to dry. Now add 1 drop of the weakly acidic ($< 0.5M$) test solution. A red brown fleck or ring is produced if thiocyanate is present.

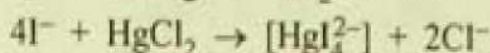
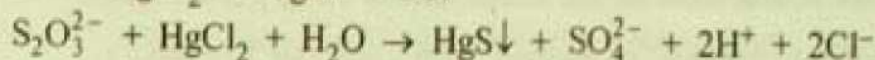
Limit of identification : 0.3γ of SCN^-

Limit of dilution : 1 : 1.6×10^5 .

(b) Thiocyanate in presence of sulfide, thiosulfate, and iodide

Iodine-azide reaction is catalysed by SCN^- , S^{2-} and $\text{S}_2\text{O}_3^{2-}$ ions and they interfere each others detection. Iodide is oxidized to iodine by Fe^{3+} ion. Brown colouration due to iodine or (I_3^- ion) spoils the FeCl_3 test of thiocyanate. Interference due to all these three ions e.g. S^{2-} , $\text{S}_2\text{O}_3^{2-}$ and I^- may be eliminated by treating the test solution with 1-2 drops of mercuric chloride solution. Sulfide is precipitated as acid insoluble black HgS . Thiosulfate reacts with

HgCl_2 precipitating black HgS with liberation of H^+ ion. Iodide is precipitated as red HgI_2 , or forms a colourless soluble complex $[\text{HgI}_4]^{2-}$ ion, which does not interfere with the test of thiocyanate. A small amount of potassium chloride is to be added to the mercuric chloride solution to prevent the hydrolysis of mercuric ion in aqueous solution. KCl and HgCl_2 react to form soluble chloro complexes, $\text{K}[\text{HgCl}_3]$ and $\text{K}_2[\text{HgCl}_4]$.



If the test solution after treatment with mercuric chloride solution is centrifuged, the centrifugate will be free from S^{2-} , $\text{S}_2\text{O}_3^{2-}$ and free I^- ions. The centrifugate may now be tested with

(i) I_2 -azide reagent (cf. p.-377)

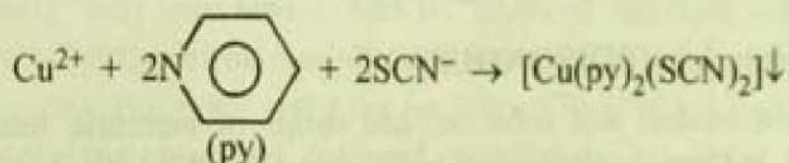
(ii) FeCl_3 reagent (cf. p.-377).

Limit of identification : 10 γ of KSCN is presene of 360 γ of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$.

(2) Copper sulfate-Pyridine reagent

When thiocyanate in neutral solution reacts with Cu(II) salt solutions containing a few drops of pyridine (py), a yellowish-green precipitate of the complex, $[\text{Cu(py)}_2(\text{SCN})_2]$, is formed. The complex dissolves in chloroform, producing an emerald green solution.

Caution : Pyridine is poisonous, excess pyridine should be avoided. It should not be inhaled.



Take 1-2 drops of 1% copper sulfate solution in a semi-micro test tube, add 2 ml of water, 1-2 drops of pyridine, 1 ml of chlorform and then a few drops of the neutral test solution. Shake the mixture thoroughly. The chlorform layer assumes a green colour if thiocyanate is present.

Limit of dilution : 1 : 5×10^4 .

5.9. Reactions of Sulfate (SO_4^{2-})

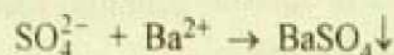
Barium, strontium and lead sulfates are insoluble. Calcium sulfate, mercuric sulfate are slightly soluble. Basic sulfates of chromium, mercury and bismuth are sparingly soluble in water but dissolve in dilute HCl and HNO_3 . Sulfates of all other metals are soluble in water.

Indication

There is practically no preliminary indicative test for sulfate, that can be directly applied on the solid sample. It is convenient to test for sulfate with the aqueous extract or the Na_2CO_3 extract or the Na_2CO_3 fusion extract of the sample. In any case, the test solution should be acidified with dil. HCl or dil. HNO_3 , for not to be mistaken, since sulfites, phosphates and carbonates also form precipitates with the reagents used for testing sulfate.

(1) Barium chloride solution

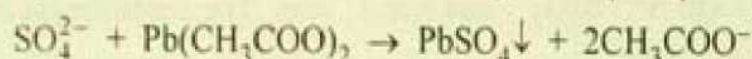
Take 1 *ml* of the acidified test solution in a semi-micro test tube, add 1 drop of BaCl₂ solution (0.25*M*). A heavy white precipitate of BaSO₄ appears.



The precipitate is insoluble in hot dilute HCl or HNO₃ (distinction from CO₃²⁻, SO₃²⁻ and PO₄³⁻) but moderately soluble on boiling with conc. HCl or HNO₃.

(2) Lead acetate solution (0.25*M*)

To 1 *ml* of the test solution acidified with dil. HNO₃ (not dil. HCl, since PbCl₂ is sparingly soluble), add 1-2 drops of lead acetate solution. Heavy white precipitate of lead sulfate appears.



The precipitate is soluble in hot conc. H₂SO₄, hot solutions ammonium acetate, ammonium tartrate and sodium acetate.

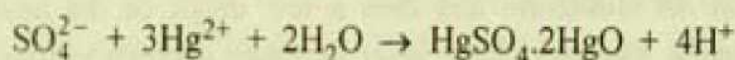
(3) Silver nitrate solution (20%)

To 1-2 drops of the concentrated test solution, acidified with dil. HNO₃ (not dil. HCl, as AgCl is sparingly soluble), add drops of 20% silver nitrate solution. White crystalline precipitate of silver sulfate (Ag₂SO₄) appears.

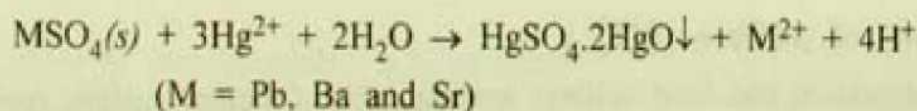


(4) Mercuric nitrate solution (POISONOUS)

To 1-2 drops of the neutral test solution, add drops of mercuric nitrate solution (not containing much acid). Yellow precipitate of basic mercury (II) sulfate appears at once and the resulting mixture becomes acidic :

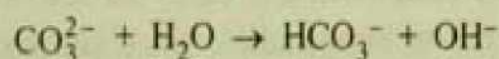
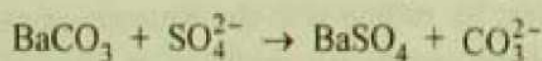


This test is so sensitive for sulfate that it is responded by even suspensions of lead, barium and strontium sulfates :



(5) Barium carbonate-Phenolphthalin test

Sparingly soluble barium carbonate reacts with soluble sulfates, precipitating insoluble barium sulfate, setting free carbonate ion in aqueous solution. Hydrolysis of carbonate ion gives an alkaline solution, which turns colourless phenolphthalin indicator pink coloured,



Only silicofluoride (SiF_6^{2-}) ion interferes. The test solution must be neutral. If Na_2CO_3 extract or Na_2CO_3 fusion extract is used, it should be neutralized with dil. HCl. The resulting solution should be evaporated to dryness to remove any excess HCl before adding BaCO_3 .

In a small porcelain crucible mix 1 drop of the neutral test solution with 1 drop of pure BaCO_3 suspension and evaporate the mixture on a hot water bath. Add 1 drop of 1% phenolphthalin indicator solution in (1:1) ethanol-water mixture. A pink colouration appears if sulfate is present. Compare with a blank, since BaCO_3 shows slight alkalinity.

Limit of identification : 5γ of Na_2SO_4

Limit of dilution : 1 : 10,000

Confirmation

(1) Potassium permanganate-Barium sulfate test

When Ba^{2+} ion and SO_4^{2-} ion react to produce the white precipitate of BaSO_4 in presence of permanganate (MnO_4^-) ion, barium sulfate includes some permanganate ions in its lattice, ultimately producing a violet precipitate. Permanganate ion thus retained in the crystal lattice of BaSO_4 , is rendered unreactive and quite resistant to all reducing agents, which normally reduce permanganate instantaneously, e.g. oxalic acid, H_2O_2 , SO_2 -water, sodium nitrite etc. On the other hand, the purple colour of the excess permanganate ion in the solution is discharged by these reagents, rendering the violet coloured $\text{BaSO}_4\text{-KMnO}_4$ precipitate clearly visible.

Take 3-4 drops of the test solution in a semi-micro test tube, add dil. HNO_3 (not dil. HCl as HCl reduces MnO_4^- ion) until acidic. Add 1-2 drops of saturated potassium permanganate solution and finally 1-2 drops of barium nitrate solution (0.25 M) (not barium chloride as Cl^- ion reduces MnO_4^- ion). Place the test tube on a hot ($70\text{-}80^\circ\text{C}$) water bath for 7-8 minutes. Centrifuge and remove the clear pink coloured centrifugate. Wash the residue with water by centrifugation. A violet coloured residue is formed if SO_4^{2-} is present. Add 1-2 drops of H_2O_2 or a crystal of oxalic acid and a drop of dil. HNO_3 to the residue. The pink colour of MnO_4^- in the residue is not discharged. On the other hand, add 1-2 drops of H_2O_2 or 1-2 crystals of oxalic acid to the pink coloured centrifugate, warm slightly. Pink colour of MnO_4^- is discharged.

Limit of identification : 2.5γ of H_2SO_4

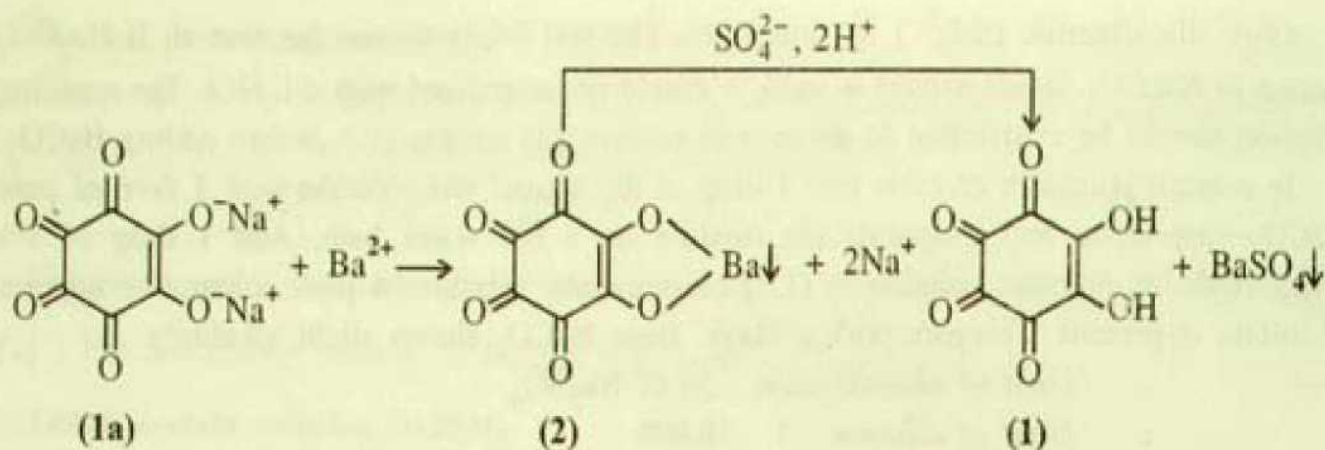
Limit of dilution : 1 : 2×10^4

(2) Test with barium rhodizonate

Reagents : (i) 0.1% solution of sodium rhodizonate.

(ii) 0.25M barium chloride solution.

Ba^{2+} ion reacts with rhodizonic acid (1) or sodium rhodizonate (1a) to form red-brown precipitate of barium rhodizonate (2). If the reaction is carried out on a filter paper, the precipitate of barium rhodizonate is stable towards dilute HCl (or HNO_3), but sulfuric acid and sulfate salts cause immediate decolourization, due to the formation of insoluble barium sulfate.



(a) Place one drop of barium chloride solution on a drop reaction paper and allow the spot to dry. Add 1 drop of 0.1% sodium rhodizonate to the spot. A red fleck is formed. Now add 1 drop of slightly acidic or neutral test solution. The red fleck of barium rhodizonate disappears if sulfate is present.

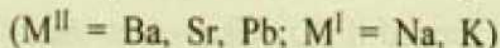
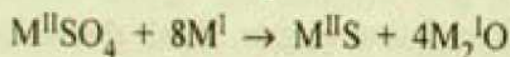
(b) Alternatively, place 1 drop of barium chloride and 1 drop of 0.1% sodium rhodizonate on a spot plate and stir with a glass rod. A red-brown coloured suspension of barium rhodizonate is formed. Add a drop of the neutral or slightly acidic test solution. The red-brown colour is discharged if sulfate is present. Compare with a blank.

Limit of identification : 5γ of Na₂SO₄

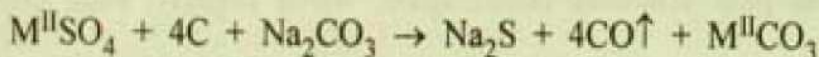
Limit of dilution : 1 : 10,000

(3) Test for Insoluble Sulfates (Reductive fusion tests)

(a) Insoluble sulfates such as BaSO₄, SrSO₄, PbSO₄ are conveniently reduced to sulfide by fusing with metallic sodium or potassium in a fusion tube.



(b) Alternatively, the insoluble sulfate may be reduced to sulfide with charcoal in a matrix of molten NaKCO₃ (*fusion mixture*):



The fused mass is extracted with water and the solution is tested for sulfide with the following reagents (*cf.* Sect. 5.7).

(i) I₂-azide reaction :

Discharge of iodine colour with evolution of N₂ gas.

(ii) Sodium nitroprusside :

Violet colouration is produced.

(iii) Lead acetate-acetic acid :

Black precipitate of PbS is formed.

Sulfite, thiosulfate, thiocyanate are transformed to sulfide through these reductive fusion reactions. Sulfide and all these anions are to be removed before subjecting the sample for

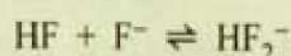
reductive fusion reaction for detection of sulfate. But if the reductive fusion is carried out with the dried BaSO_4 residue obtained on treatment of the test solution with barium chloride solution in presence of HCl , interference due to S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ are eliminated, since barium salts with these anions are soluble in dil.HCl .

Limit of identification : 36γ of BaSO_4

Limit of dilution : 1:1400

5.10. Reactions of Fluoride (F^-), Bifluoride (HF_2^-)

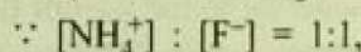
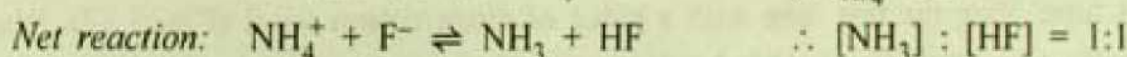
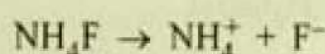
Fluorides of lead, barium, copper, iron (III), lithium are slightly soluble and those of other alkaline earth metals are insoluble. Sodium, potassium and ammonium fluorides are soluble in water. Hydrogen fluoride (HF) is highly soluble in water and its aqueous solution is moderately acidic,



Consequently, aqueous solutions of normal fluorides (NaF , KF) are alkaline due to hydrolysis of F^- ion,



Ammonium fluoride, NH_4F , in aqueous solution is nearly neutral due to hydrolysis of both NH_4^+ and F^- ions :



$$K_{\text{NH}_4}^H \cdot K_{\text{HF}}^H = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} \cdot \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = [\text{H}^+]^2$$

$$\therefore p[\text{H}] = \frac{1}{2}(pK_{\text{NH}_4}^H + pK_{\text{HF}}^H) = \frac{1}{2}(9.2 + 3.2) = 6.1$$

Alkali metal hydrogen fluorides (KHF_2) and ammonium bifluoride (NH_4HF_2) may be regarded as 1:1 mixtures of salts (KF or NH_4F) and HF , i.e. a (1:1) mixture of a weak acid (HF) and its salt (KF or NH_4F). NH_4^+ ion is too weakly acidic ($pK_{\text{NH}_4}^H = 9.2$) in comparison to HF ($pK_{\text{H}}^H = 3.2$). So, NH_4^+ ion practically remains neutral. Thus, the $p[\text{H}]$ of an aqueous solution of ammonium bifluoride will be in the moderately acidic region.

$$p[\text{H}] = pK_{\text{HF}}^H + \log \frac{[\text{F}^-]}{[\text{HF}]} = 3.2 + \log \frac{[\text{F}^-]}{[\text{HF}]} = 3.2$$

$$(\because [\text{F}^-] = [\text{HF}])$$

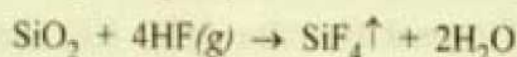
Therefore, examination of acid - base nature of the aqueous extracts of salts of HF will give information as to whether the fluoride salt is a normal fluoride or a acid fluoride (or bifluoride).

Indication

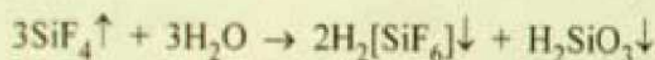
(1) Hot concentrated sulfuric acid

(CAUTION : Test to be conducted in FUME CUPBOARD)

As HF is a volatile weak acid, fluoride/hydrogen fluoride salts are decomposed on treatment with hot conc. H_2SO_4 , when hydrogen fluoride (HF) is set free. HF has a profound tendency to attack glass and other silicate materials. If the test is conducted in a glass test tube, the liberated HF tends to adhere to the wall of the test tube, forming bubbles while moving upward and reacts with the silicate (or silica) materials of glass, producing silicon tetrafluoride gas, resulting in an oily appearance in the test tube,



Now, if a drop of water at the head of a glass rod is held in the issuing vapour, the water drop becomes opaque due to the formation of silicic acid (H_2SiO_3) and hexafluorosilicic acid, $\text{H}_2[\text{SiF}_6]$.



Note : Gaseous hydrogen fluoride exists as dimeric species (H_2F_2) at room temperature and as monomeric species (HF) at elevated temperature (90°C).

(a) Mix small amount ($< 0.1\text{g}$) of the solid sample with 3-4 drops of conc. H_2SO_4 in a semi-micro test tube. Plug the test tube with a piece of clean cotton wool (Fig. 3.27). Warm the test tube gently on a small flame. Oily bubbles adhering to the wall of the test tube appear. Hold a drop of water at the head of a glass rod or a dropper (Fig. 3.27b) to the issuing vapour. The water drop turns opaque.

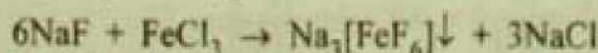
(b) In a slight modification of the above test, add a small crystal of $\text{K}_2\text{Cr}_2\text{O}_7$ along with conc. H_2SO_4 and warm gently as before. Formation of oily bubbles are clearly visible against the dark brown back ground of the resulting solution.

Reactions of fluoride ion in solution

Aqueous extract or Na_2CO_3 extract or Na_2CO_3 fusion extract after neutralization may be tested for fluoride.

(1) Ferric chloride solution

To 1 ml of concentrated neutralized test solution add a few drops of FeCl_3 solution (0.5M). A white crystalline precipitate appears due to the formation of hexafluoroferrate (III) salts:



The precipitate does not respond to any reaction of Fe(III), except on acidification.

(2) Calcium chloride solution

To 1 ml of concentrated neutralized test solution of the sample, add a few drops of calcium chloride solution (0.5M). White slimy precipitate of calcium fluoride (CaF_2) appears.



The precipitate is slightly soluble in acetic acid but more soluble in dilute hydrochloric acid.

(3) Silver nitrate solution

No precipitation occurs, since silver fluoride is soluble.

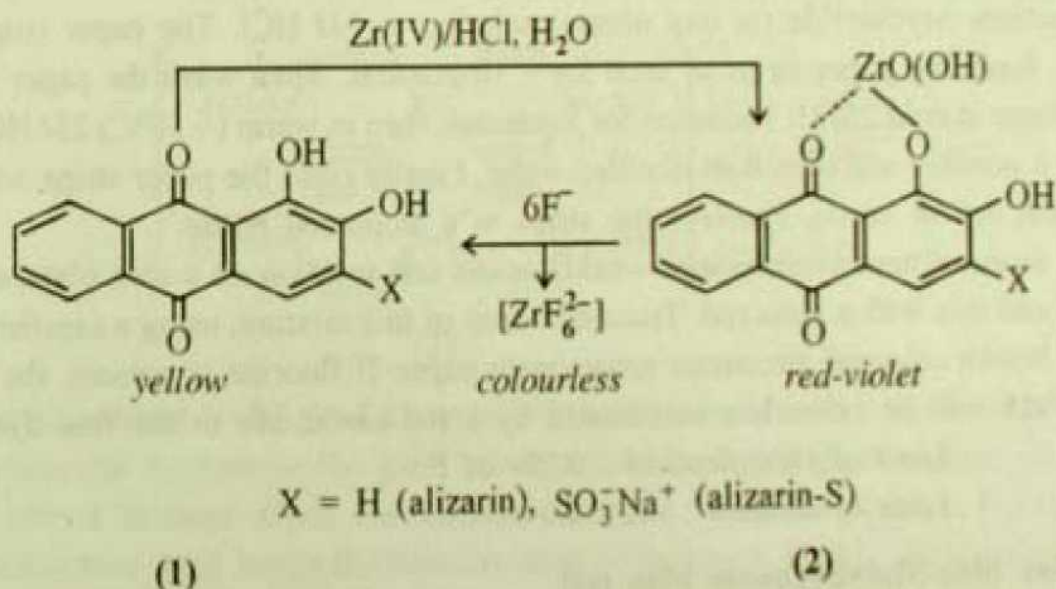
Confirmation

(1) Zirconium-Alizarin lake test

Reagents :

- (i) Zirconyl chloride (0.1M) : Dissolve 3.2g of $\text{ZrO}_2\text{Cl}_2 \cdot 8\text{H}_2\text{O}$ in 10 ml of 2M HCl solution and dilute to 100 ml.
- (ii) 0.1% solution of alizarin-S : Dissolve 0.1g of sodium alizarin sulfonate monohydrate, $\text{C}_{14}\text{H}_7\text{O}_4 \cdot \text{SO}_3\text{Na} \cdot \text{H}_2\text{O}$ in 100 ml of water.

Zirconium salts react with alizarin red-S or alizarin (1) reagent in hydrochloric acid medium to produce a redish-violet adsorption product, i.e, zirconium-alizarin lake (2). Upon addition of a soluble fluoride salt, the red-violet colour is discharged, as the adsorption complex is decomposed due to the formation of hexafluorozirconate (IV), $[\text{ZrF}_6]^{2-}$ ion, arising from strong hard-hard interaction between Zr(IV) and F^- ions.



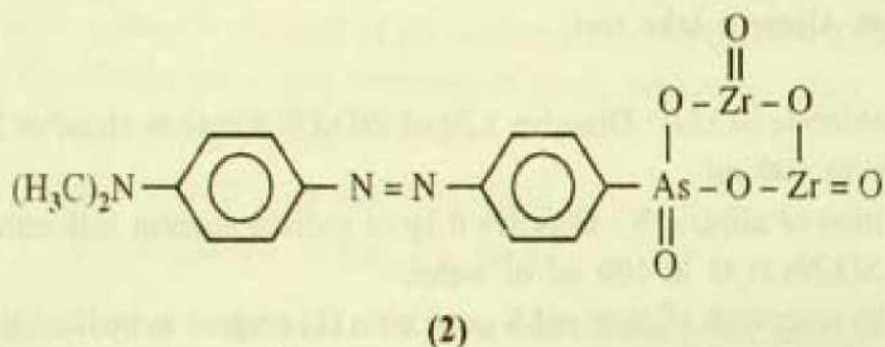
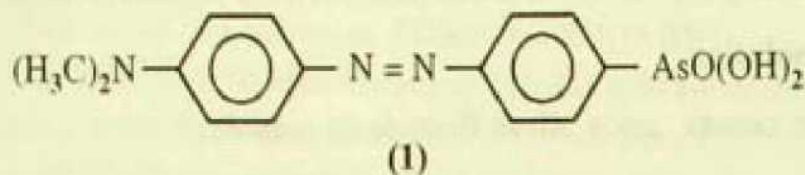
On a spot plate, mix 2 drops of 0.1% alizarin-S (or alizarin) reagent, 2 drops of 0.1 (M) zirconyl chloride (or nitrate) solution and a drop of dil. HCl. A redish-violet colouration or a precipitate is formed. Add drops of the slightly acidic test solution and mix with a glass rod. The red-violet colour is discharged leaving a clear yellow solution of the free reagent, if fluoride is present.

Limit of identification : 1γ of F^- ion

Limit of dilution : $1:5 \times 10^4$.

(2) Zirconium-Azoarsonate test

Acid solution of Zr(IV) salts react with the red coloured reagent, *p*-dimethylaminoazophenyl arsonic acid (1), producing a brown precipitate, probably of the complex (2). On addition of a soluble fluoride salt, Zr(IV) produces colourless $[\text{ZrF}_6]^{2-}$ complex ion, setting free the red coloured reagent.



Reagent : Zirconium azoarsonate paper :

Prepare a 0.025% solution of *p*-dimethylaminoazophenyl arsonic acid in 9:1 ethanol : HCl medium. Soak strips of Whatman No. 1 filter paper in this solution and allow the papers to dry in air. The filter paper strips are coloured bright red. Now place the filter papers in a 0.01% zirconium oxychloride (or oxy nitrate) solution in 1M HCl. The paper strips at once turn brown. Keep the paper strips as such for ~ 10 minutes. Then wash the paper strips first by placing them in cold 2M HCl solution for 5 minutes, then in warm (~ 55°C) 2M HCl solution for another 5 minutes and then with distilled water. Finally rinse the paper strips with alcohol and ether and dry in vacuo. Preserve the strips in a stoppered bottle.

Place 3 drops of neutral/alkaline/or weakly acidic test solution on a spot plate, add 1 drop of 2 M HCl and mix with a glass rod. Transfer 1 drop of this mixture, using a capillary dropper, to the light brown coloured zirconium azoarsonate paper. If fluoride is present, the middle of the moist fleck will be colourless surrounded by a red circle due to the free dye stuff.

Limit of identification : 0.25γ of F^-

Limit of dilution : $1:2 \times 10^5$

(3) Benzidine blue-Molybdeneum blue test

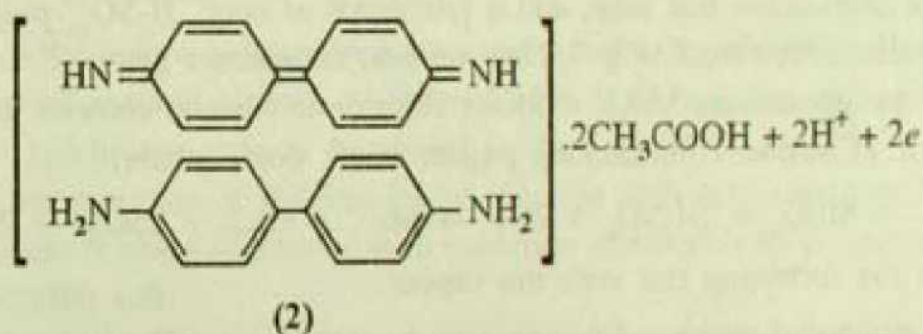
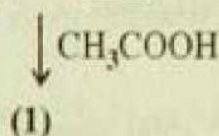
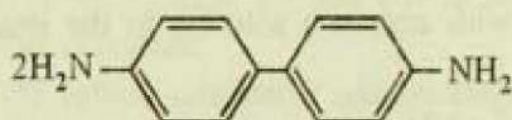
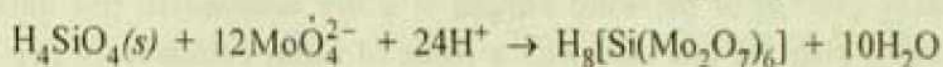
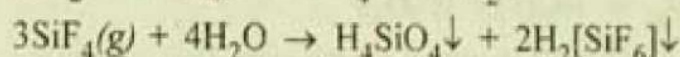
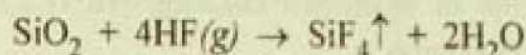
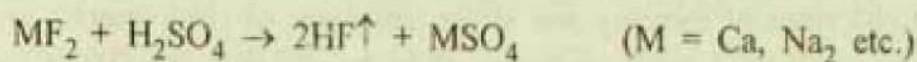
Reagents :

(i) Ammonium molybdate : Dissolve 1.5g of ammonium molybdate in 30 ml of water and pour this solution into 10 ml of conc. HNO_3 (Sp. gr. = 1.2).

(ii) Benzidine : 1% solution of benzidine in 10% acetic acid.

Both soluble and insoluble fluoride salts on warming with concentrated sulfuric acid in presence of silica (SiO_2) or in a glass test tube, produce volatile silicon tetrafluoride, SiF_4 , gas (b.p.-65°C). If this SiF_4 gas is absorbed in a drop of water, it undergoes hydrolysis to

produce the precipitate of silicic acid (H_2SiO_3 or H_4SiO_4) and hexafluorosilicic acid $\text{H}_2[\text{SiF}_6]$, which render the water drop opaque (discussed before). When allowed to react with ammonium molybdate in presence of nitric acid, both these products are converted to silicomolybdic acid, $\text{H}_8[\text{Si}(\text{Mo}_2\text{O}_7)_6]$. Simple molybdic acid, (MoO_3 or H_2MoO_4) does not oxidize benzidine (1) to benzidine blue (2), but silicomolybdic acid does so in acetic acid medium with concurrent reduction of itself into molybdenum blue, which is a mixture of varying proportions of Mo (VI) and Mo (V) oxides [chief constituent of molybdenum blue is $\text{Mo}_4\text{O}_{11} = \text{Mo}_2\text{O}_5 \cdot 2\text{MoO}_3$]. Silica is to be used in excess to prevent the loss of HF.



Mix a small amount (~ 0.1g) of the powdered solid sample with 3 times its bulk of pure silica and place the mixture in the glass reaction tube having a glass stopper with bulb or a glass dropper at its head. Open the reaction tube, add 3-4 drops of conc. H_2SO_4 . Place a piece of clean cotton wool inside the tube avoiding contact with H_2SO_4 . Hold a drop of water at the bulb head of the glass stopper or the dropper and fix the same upon the reaction tube (Fig. 3.27b). Warm the reaction mixture gently for a few minutes avoiding bumping, until the water drop appears opaque. Now transfer the opaque water drop to a spot plate, add 1 drop of nitric acid, 1 drop of ammonium molybdate and mix with a glass rod. Add 1 drop of benzidine reagent and a crystal of sodium or ammonium acetate. Blue colouration appears very shortly if fluoride is present in the sample. Run a blank test.

Limit of identification : 1γ of F^-

Limit of dilution : 1 : 5×10^4 .

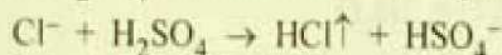
5.11 Reactions of Chloride (Cl^-)

Silver chloride (AgCl), mercurous chloride (Hg_2Cl_2), cuprous chloride (CuCl), bismuth oxychloride (BiOCl), antimony oxychloride (SbOCl), mercuric oxychloride [Hg_2OCl_2] are insoluble in water. Lead chloride (PbCl_2) is sparingly soluble in cold water but readily soluble in hot water. Chlorides of all other metals are soluble in water.

Indication

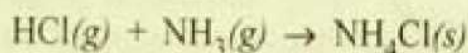
(1) Hot concentrated sulfuric acid

Except the chlorides of mercury and silver, chlorides of other metals are decomposed on warming with conc. H_2SO_4 , with evolution of hydrogen chloride (HCl) gas,



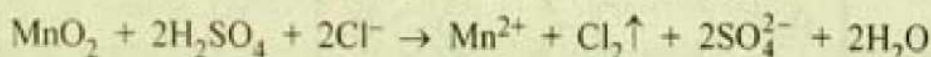
Place a small quantity ($<0.1\text{g}$) of the solid sample in a dry semi-micro test tube, add a few drops of conc. H_2SO_4 , plug the test tube with a piece of clean cotton wool (Fig. 3.27a) and heat gently. White vapour of HCl appears. Perform the following tests with the vapour.

- Hold a moistened blue litmus paper to the issuing gas. Blue litmus turns red.
- Hold a glass rod moistened with ammonia solution to the issuing gas. White cloud of ammonium chloride is formed.



2. Hot concentrated $\text{H}_2\text{SO}_4 + \text{MnO}_2$

Mix a small quantity of the powdered solid sample with its equal quantity of manganese dioxide in a semi-micro test tube, add a few drops of conc. H_2SO_4 , plug the test tube with a piece of clean cotton wool (Fig. 3.27a) and heat the mixture gently. Greenish-yellow vapour of chlorine gas appears as MnO_2 oxidizes chloride to liberate chlorine and itself is reduced to Mn^{2+} salt. (**Caution** : Suffocating pungent smell, don't inhale).



Perform the following test with the vapour.

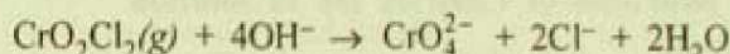
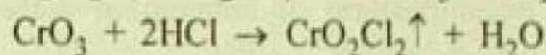
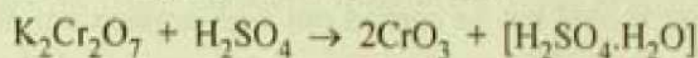
Hold a moistened starch-iodide paper to the issuing gas. The paper turns blue, as iodide is oxidized to iodine by Cl_2 and iodine forms a blue coloured adsorption product with starch.



3. Chromyl chloride test

Mix a small amount ($<0.1\text{g}$) of the powdered sample with three times its bulk of powdered potassium dichromate in a semi-micro reaction tube fitted with a dropper with aid of a cork or glass stopper having a capillary receiver tube at its head (Fig. 3.29b). Add a few drops of conc. H_2SO_4 and fix the stopper accordingly with a few drops of $2M$ NaOH solution at its capillary head. Heat the mixture gently avoiding bumping. The drop of NaOH solution held in the capillary head turns yellow coloured if chloride is present in the sample. Conc. H_2SO_4 reacts with chloride salts to produce HCl and with dichromate to produce chromic acid, CrO_3 .

In presence of conc. H_2SO_4 , chromic acid reacts with HCl to produce deep red vapours of chromyl chloride (CrO_2Cl_2), which is absorbed in the NaOH solution to produce yellow solution of chromate (CrO_4^{2-}).



Perform the following tests with the yellow solution of sodium chromate:

(i) Place 1 drop of the yellow solution on a spot plate, add drops of acetic acid until acidic and then add 1 drop of barium chloride. Yellow precipitate of barium chromate is formed.



Note : Lead acetate is not suitable for this test as white precipitate of PbCl_2 may mask the yellow colour of lead chromate.

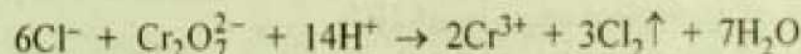
(ii) Place a drop of the yellow solution of sodium chromate on a spot plate, add dil. H_2SO_4 until acidic and finally add a drop of diphenylcarbazide reagent (*cf.* Sect. 4.13). An intense violet colouration is produced.

Limit of identification : 0.3γ of chloride

Limit of dilution : 1 : 1.5×10^5 .

(iii) Take 1 drop of the yellow solution in a semi-micro test tube, add drops of dil. H_2SO_4 (2N) until acidic, 1 ml of isoamyl alcohol, 4-5 drops 10% H_2O_2 solution and shake gently. A blue colour due to perchromic acid is developed in the organic layer.

Note : (i) Under the condition of the reaction of chloride with dichromate and hot conc. H_2SO_4 , some chlorine gas is always formed due to oxidation of chloride by dichromate, which is reduced to green Cr(III) solts :



(ii) Bromide and iodide are oxidized by acid-dichromate to free halogens, which react with NaOH solution to give colourless solutions of oxyhalides. If the $[\text{I}^-] : [\text{Cl}^-]$ ratio exceed 1:15, formation chromyl chloride is prevented, instead chlorine is evolved. Iodine is oxidized by chromic acid to iodic acid. In presence of hot conc. H_2SO_4 , iodic acid (HIO_3) oxidizes chloride to set free chlorine and regenerates iodide and the new cycle of reaction starts. As a result, chromyl chloride test fails.

(iii) Fluorides react similar to the chlorides, forming volatile chromyl fluoride (CrO_2F_2), which also reacts with water and NaOH solution to produce yellow colouration due to chromate. So, fluoride if present, must be removed.

(iv) Nitrate and nitrites also interfere by producing volatile nitrosyl chloride (NOCl).

(v) Chlorides of Pb, Ag, Sb and Sn are only partly converted to chromyl chloride, as these are very weakly dissociated to form chloride ion. Mercury chlorides are so less dissociated that they do not respond to chromyl chloride test.

(vi) This test must not be performed in presence of chlorates, as dangerously explosive chlorine dioxide (ClO_2) may be formed.

(vii) Chromyl chloride test should not be carried out with ammonium dichromate in place of potassium dichromate, as thermal decomposition of ammonium dichromate may cause explosion and fire.

Reactions of Chloride ion in solution

Aqueous extract or Na_2CO_3 extract of the sample should be neutralized with dil. HNO_3 or aq-NH_3 solution as required.

(1) Silver nitrate solution

(a) To 1-2 drop of neutral or weakly acidic (HNO_3) solution containing chloride ion, add 1 drop of silver nitrate solution (0.1M). Curdy white precipitate of silver chloride appears. The precipitate coagulates on boiling.



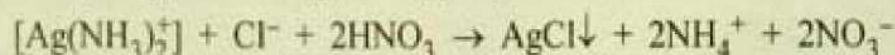
Centrifuge, reject the centrifugate, divide the precipitate into three parts and perform the following tests :

(i) Add a few drops of dilute aqueous ammonia or ammonium carbonate solution to the precipitated AgCl .

The precipitate dissolves, giving a colourless solution due to the formation of $[\text{Ag}(\text{NH}_3)_2]^+$ complex ion.



Add a few drops of dilute HNO_3 to the ammoniacal solution containing the $[\text{Ag}(\text{NH}_3)_2]^+$ complex. Curdy white precipitate of AgCl reappears,

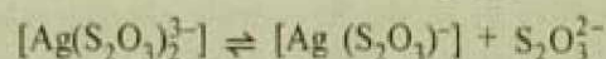
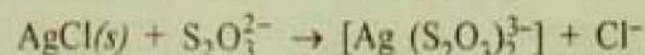


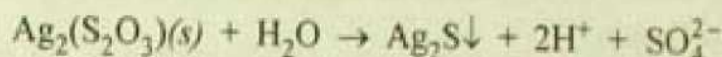
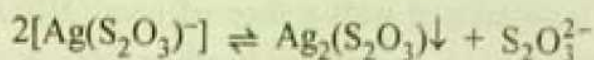
Limit of identification : 1γ of HCl

Limit of dilution : 1 : 5×10^4 .

CAUTION : Discard the ammoniacal solution of $[\text{Ag}(\text{NH}_3)_2]^+$ immediately after the test to avoid explosion due to the formation of silver nitride, Ag_3N (*fulminating silver*). Don't throw the solution into the waste paper basket, since decomposition of dry Ag_3N may cause fire. Wash out the solution with running water.

(ii) Add a few drops of concentrated sodium thiosulfate solution ($\sim 0.5M$) to the precipitated silver chloride. The precipitate dissolves giving a clear solution, which gradually turns dark on standing, and black precipitate of Ag_2S appears rapidly on warming.





(iii) Add 1 drop of sodium arsenite solution to another part of the precipitated silver chloride. The white precipitate of AgCl gradually transforms into a yellow precipitate of silver arsenite (Ag_3AsO_3).



Silver bromide and silver iodide do not respond to this test. By this reaction one may differentiate chloride from bromide and iodide.

Note : Bromide, iodide and thiocyanate are also precipitated as their silver salts when treated with AgNO_3 solution in dil HNO_3 medium. While AgCl and AgSCN dissolves in dilute ammonia solution, AgBr dissolves in concentrated ammonia. AgI is insoluble even in concentrated ammonia.

(b) Testing chloride in presence of other halides

Silver nitrate test can be made specific for chloride ion by eliminating bromide, iodide and thiocyanate from the solution. This is achieved by treating weakly acidic (acetic acid or HNO_3) solution containing these ions with hydrogen peroxide in presence of 8-hydroxyquinoline (oxine). H_2O_2 oxidizes bromide and iodide to free halogen molecules, which halogenate 8-hydroxyquinoline to its trihalo derivatives that precipitate out and do not react with silver nitrate solution. In weakly acidic medium, H_2O_2 converts thiocyanate to sulfuric acid and hydrogen cyanide which is decomposed by acids. Thiocyanogen $(\text{SCN})_2$, produced if any, reacts with 8-hydroxyquinoline in the same manner as bromine and iodine. Chloride remains practically unaffected on the addition of H_2O_2 . The following procedure is specific for chloride in presence of other halides.

Take a drop of the test solution in a semi-micro test tube, add a drop of oxine reagent and warm slightly. Add a drop of H_2O_2 and a drop of dilute HNO_3 . Warm gently for ~ 2-3 minutes, centrifuge if necessary. Add 1 drop of 1% AgNO_3 solution to the centrifugate. A white precipitate or turbidity appears if chloride is present.

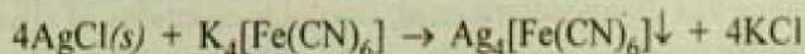
Reagents : (i) 2% solution of oxine in (1:4) acetic acid.

(ii) 2 parts of "20-volume" H_2O_2 and 1 part of dilute (5M) acetic acid.

Silver chloride may be isolated from other silver halides by warming the mixture of halides with a (4:1) mixture of saturated ammonium carbonate and ammonia, in which AgCl dissolves completely and may be reprecipitated on acidification with HNO_3 . Only traces of AgBr dissolves in this $(\text{NH}_4)_2\text{CO}_3/\text{NH}_3$ mixture, AgI remains completely insoluble.

(2) Identification of silver chloride

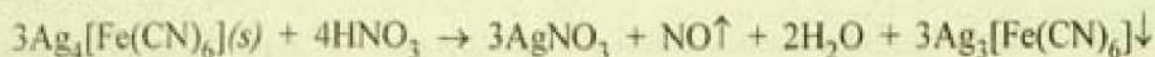
If precipitated AgCl is warmed with potassium ferrocyanide solution, it is transformed into more insoluble silver ferrocyanide, although no visible change takes place as both silver chloride and silver ferrocyanide are white solids.



$$pK_{sp} = 9.75$$

$$pK_{sp} = 40.8$$

But if the precipitate of AgCl is moistened with a drop of conc. HNO_3 and then treated with $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution, silver ferrocyanide is oxidized to silver ferricyanide, and the colour changes from white to red brown.



Other silver halides react with potassium ferrocyanide and nitric acid in analogous manner.

(3) Test with silver carbonate

Neutral solution of halides react with silver carbonate to precipitate silver halides. Carbonate ion set free, undergoes hydrolysis, giving an alkaline solution which turns colourless phenolphthalin red.



Place a grain of silver carbonate plus one drop of phenolphthalin indicator solution on two adjacent cavities in a spot plate. Add 1 drop of the neutral test solution in one cavity and a drop of water in the other. Mix well with glass rods. A red colouration appears in the cavity containing the test solution if a halide ion is present.

(4) Lead acetate solution

To 1 drop of neutral or weakly acidic acid test solution in a semi-micro test tube, add 1 drop of lead acetate solution. A white precipitate of lead chloride appears.



Add 1 ml of water and boil. The precipitate dissolves. Now cool the solution under tap. The precipitate reappears.

Confirmation

(1) Chromyl chloride test

(a) Perform chromyl chloride test as described before (*cf.* p-390).

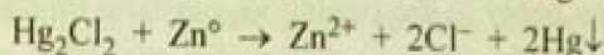
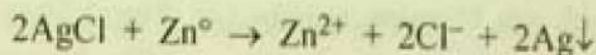
(b) Perform chromyl chloride test, using instead of 2(N) NaOH solution, a drop of 1% solution of diphenylcarbazide in ethanol inside the capillary head of the dropper of the reaction tube (Fig. 3.29b). Chromyl chloride evolved, directly reacts with the reagent, producing a violet colouration (*cf.* diphenylcarbazide test for chromium, CrO_4^{2-} Sects. 4.13, 5.18).

(2) Silver nitrate test

After oxidation of Br^- , I^- , SCN^- if any, with H_2O_2 in presence of 8-hydroxyquinoline as described before and separating any precipitate at this stage by centrifugation, add dilute HNO_3 and silver nitrate solution. A curdy white precipitate, soluble in $\text{NH}_3/(\text{NH}_4)_2\text{CO}_3$ confirms chloride.

(3) Test for chloride in insoluble chlorides

On treatment with Zn dust and dilute sulfuric acid, insoluble chlorides of silver and mercury are reduced with precipitation of the metals, setting free chloride ion in solution :



The unreacted Zn and precipitated metals are removed by centrifugation / filtration. The resulting solution should be boiled for some time to remove any H_2S that may occur due to the presence of sulfide, sulfite, thiocyanate, which produce H_2S on treatment with Zn and dil. H_2SO_4 . The resulting solution may be tested for chloride as usual. Insoluble bromide and iodide are also extracted into the solution by Zn/dil. H_2SO_4 treatment.

5.12. Reactions of Bromide (Br^-)

Bromides of most metals are soluble in water, except silver, mercury (I) and copper (I) bromides, which are insoluble and lead bromide, which is sparingly soluble in water.

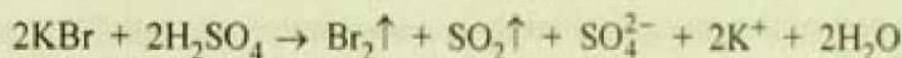
Indication

CAUTION : Perform all tests on solid bromide sample inside the **FUME CUPBOARD**

(1) Concentrated sulfuric acid

To a small quantity ($<0.1\text{g}$) of powdered sample in a semi-micro test tube, add a few drops of conc. H_2SO_4 and plug the mouth of the test tube with a piece of clean cotton wool (Fig. 3.27a).

Reddish brown vapour of bromine along with vapour of HBr (that fumes in moist air) appears, as H_2SO_4 oxidizes bromide and displaces HBr from bromide salts :

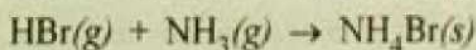
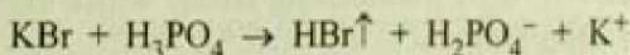


The reaction is accelerated on heating.

(2) Concentrated phosphoric acid

Take a small quantity ($<0.1\text{g}$) of the sample and 2-3 drops of conc. H_3PO_4 in a semi-micro test tube, plug the mouth of the test tube with a piece of clean cotton wool (Fig. 3.27a) and warm gently.

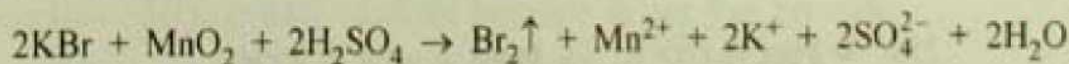
Fumes of HBr appear. Hold a glass rod moistened with ammonia solution at the issuing vapour. The vapour becomes dense cloudy due to the formation of NH_4Br .



(3) Manganese dioxide + conc. H_2SO_4

Mix a small amount ($<0.1\text{g}$) of the powdered sample with equal amount of MnO_2 in a semi-micro test tube. Add 2-3 drops of conc. H_2SO_4 , plug the test tube with a piece of clean cotton wool (Fig. 3.27a) and warm gently.

Reddish brown vapour of Br_2 appears as bromide is oxidized to Br_2 by MnO_2 in presence of H_2SO_4 (**CAUTION**).



Perform the following tests with the bromine vapour (*cf.* Fig. 3.29a) :

- (i) Hold a moistened blue litmus paper to the issuing vapour. The litmus paper is bleached.
- (ii) Hold a moistened starch - iodide paper to the issuing gas. Blue colouration appears as Br_2 oxidizes I^- to I_2 that forms a blue adsorption complex with starch.



- (iii) Hold a filter paper impregnated with fluorescein reagent to the issuing gas. A red colouration is produced as fluorescein is brominated to form eosin. (*p*-398).

Reactions of Bromide ion in Solution

Use aqueous extract or Na_2CO_3 extract after neutralization with dilute HNO_3 or dilute NH_3 solution as required.

(1) Silver nitrate solution

To 1 ml of neutral or weakly acidic test solution, add drops of dil. HNO_3 until distinctly acidic. Boil for a few minutes (to remove CO_2 , H_2S , SO_2 etc. if any, from CO_3^{2-} , S^{2-} , SO_3^{2-} and $\text{S}_2\text{O}_3^{2-}$ etc. if present), then add a few drops of silver nitrate solution. A pale yellow precipitate of AgBr is formed.



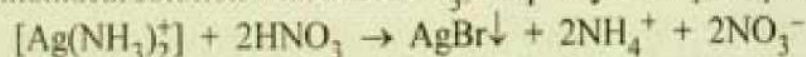
Add 1 ml of water, centrifuge, reject the centrifugate, divide the residue into three parts and perform the following tests :

- (i) Add dilute ammonia solution or saturated ammonium carbonate solution containing little ammonia to a part of the precipitate taken in a semi-micro test tube. The precipitate does not dissolve (distinction from chloride).

- (ii) To another part of the precipitate, add conc. NH_3 solution. The precipitate dissolves, giving a colourless solution due to the formation of $[\text{Ag}(\text{NH}_3)_2]^+$ complex ion.



Acidify the ammoniacal solution with dil. HNO_3 , the pale yellow precipitate of AgBr reappears.

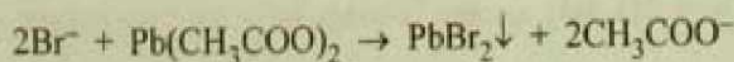


CAUTION : Discard the ammoniacal solution of silver nitrate immediately after test to avoid explosion due to the formation of Ag_3N (*fulminating silver*) which explodes readily even in wet form. (*cf.* AgNO_3 test for chloride).

- (iii) To another part of the precipitated AgBr in a semi-micro test tube, add concentrated sodium thiosulfate solution. The precipitate passes into solution. It gradually turns brown and finally becomes black due to the formation of Ag_2S . These changes are accelerated on warming. (*cf.* chloride tests for the reactions).

(2) Lead acetate solution

Take 1-2 drops of the test solution in a semi-micro test tube, add drops of dil. acetic acid until acidic and then 1 drop of lead acetate reagent. White crystalline precipitate of lead bromide appears.

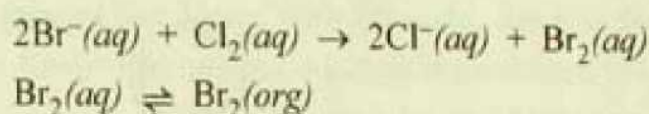


Precipitated lead bromide is soluble in boiling water. Centrifuge the mixture and discard the centrifugate. Add 1-2 ml of water to the residue and boil. The precipitate (PbBr_2) passes into solution, but reappears on cooling under running water.

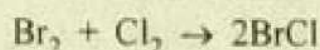
(3) Chlorine-water

It is convenient to use a dilute solution of sodium hypochlorite acidified with dil. HCl , which may be considered as hypochlorous acid (HOCl) solution.

Take 1 ml of the neutral or weakly acidic (dil. HNO_3 or dil. acetic acid) test solution and 1 ml of chloroform in a semi-micro test tube. Add 1 drop of chlorine-water (*cf.* Sect. 3.3) and shake. A redish brown colour of the organic layer indicates bromide. Cl_2 -water oxidizes Br^- to set free Br_2 , which is extrated into the chloroform layer as it is more soluble in CHCl_3 than in water.



Add a few more drops of Cl_2 -water, and shake. The redish brown colour of the organic layer gradually fades out to a pale yellow colour, due to the formation of bromine monochloride.



(4) Potassium dichromate + conc. H_2SO_4

Unlike chloride salts, bromides do not form chromyl bromide, as bromide is oxidized to bromine by dichromate in acid medium.

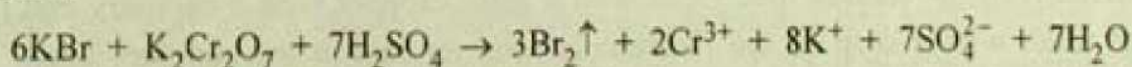
Take a small amount ($<0.1\text{g}$) of the powdered sample with an equal amount of dry $\text{K}_2\text{Cr}_2\text{O}_7$ and a few drop of conc. H_2SO_4 in a semi-micro reaction tube (Fig. 3.29b) fitted with a glass dropper having a capillary head at its end. Perform the following tests with this arrangement.

(i) Attach a drop of NaOH solution ($\sim 2M$) at the capillary head and fix the stopper at the mouth of the reaction tube with the aid of a rubber cork. Heat the mixture gently for a few minutes.

The drop of NaOH solution does not assume yellow colour (distination from Cl^- and F^-).

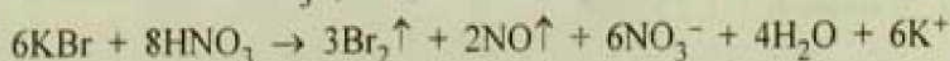
(ii) Attach 1 drop of 1% solution of diphenylcarbazide in alcohol at the cappillary head, fix the stopper at the mouth of the reaction tube as before and warm the mixture slightly. No violet colouration is produced (differen from chloride) (*cf.* Sects. 4.13, 5.18).

The above two test fail, as the issuing vapor does not contain any chromium (VI) compound (i.e. chromyl bromide), since dichromate oxidizes bromide to bromine under the condition of the experiment :



(5) Concentrated nitric acid

Hot concentrated HNO_3 ($>8M$) oxidizes bromide to set free bromine,

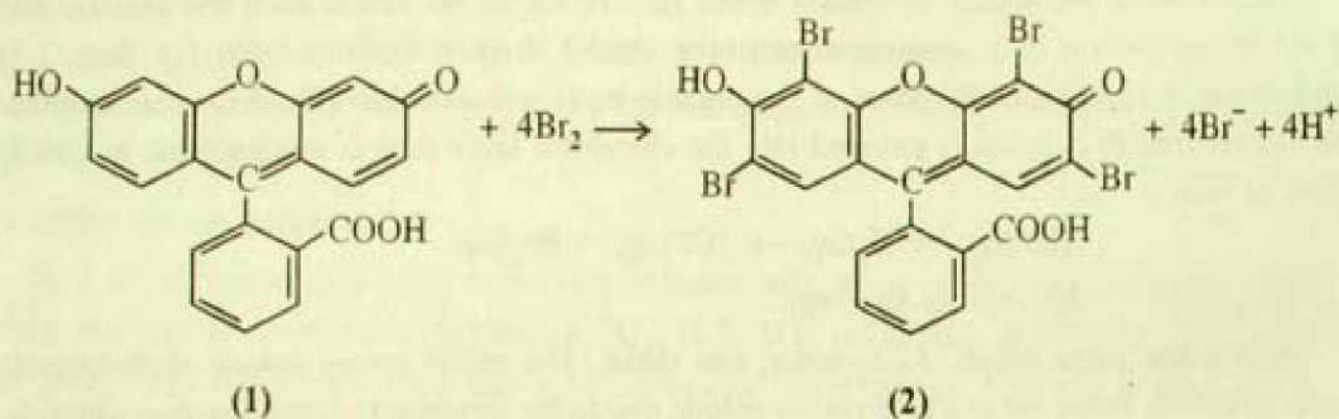


Confirmation

(1) Fluorescein test

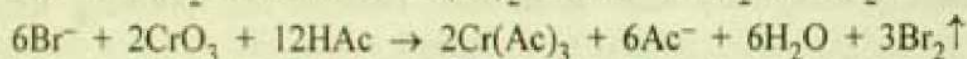
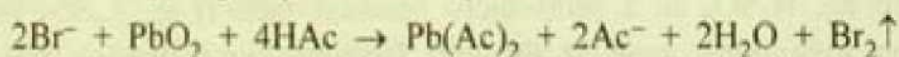
Reagent : Saturated solution of fluorescein in (1:1) ethanol-water medium.

Free bromine resulting from oxidation of bromide by a suitable oxidizing agent (PbO_2 , CrO_3 , H_2O_2) reacts with yellow coloured fluorescein (1) and brominates it to red coloured tetrabromo fluorescein or eosin (2).



Filter paper impregnated with fluorescein reagent has a yellow colour, and turns red on coming in contact with Br_2 vapour. Chlorine tends to bleach the reagent and iodine forms red violet coloured tetraiodofluorescein or erythrosin, hence, Cl^- and I^- should be absent, or if present, these should be rendered unreactive.

For generation of free Br_2 from bromide, it is best to warm the sample with lead dioxide, or chromic acid, or hydrogen peroxide in presence of acetic acid (HAc) :



(a) If PbO_2 is used as the oxidant, chloride is not oxidized, however, bromide and iodide are oxidized to the corresponding halogens. H_2O_2 can even oxidize iodide to iodate and eliminates the interfering action of iodide. The test is best accomplished in the following procedures.

Place 1-2 drop of neutral or weakly acidic (acetic acid) test solution along with a few particles of lead dioxide and $\sim 1 \text{ ml}$ of acetic acid (or a few drop of chromic acid) in a semi-micro reaction tube having a funnel stopper and a filter paper (Whatman No. 1) impregnated with fluorescein solution laid over the funnel (Fig. 3.30b). Warm the contents gently inside a **FUME CUPBOARD**. Depending upon the amount of bromide present, a red circular fleck is formed on the yellow reagent paper.

Alternatively, a reaction tube fitted with a glass dropper with a capillary end (Fig. 3.29b) may be used, with a drop of the fluorescein solution held at the capillary head. The yellow colour of the reagent changes to red in contact with bromine.

Limit of identification : 2γ of Br_2

Limit of dilution : $1:2.5 \times 10^4$.

(b) Bromine may be liberated from bromide by H_2O_2 and the following procedure is recommended for detection of bromide.

Take 1-2 drops of the neutral or weakly acidic (acetic acid) test solution on a clean porcelain crucible, add 1 drop of 1% alcoholic fluorescein reagent using a capillary dropper and 1 drop of a 10:1 mixture of glacial acetic acid and 30% H_2O_2 . Place the crucible on a hot water bath (inside a **FUME CUPBOARD**) and evaporate the mixture to dryness. A pink to red colour appears if bromide is present. Run a blank test using a drop of water in place of the test solution.

Limit of identification : 0.3γ of Br_2

Limit of dilution : 1:1.65×10⁵.

(c) Detection of bromide in presence of iodide

If iodide is also present along with bromide, the test for bromide has to be carried out on the filter paper. Under this condition iodide is oxidized to iodate by H_2O_2 , whereas, bromide is oxidized to bromine, which is absorbed by the filter paper and reacts with the reagent if the filter paper is impregnated with it.



Prepare an oxidizing mixture by mixing 2 parts of 6% H_2O_2 with 1 part of glacial acetic acid on a spot plate. Place 1 drop of neutral or weakly acidic (acetic acid) test solution on a Whatman No. 1 filter paper strip and allow the spot to dry. Add one drop of the oxidizing mixture covering the spot of the test solution and allow the paper to dry. If iodine colour is still visible, repeat the treatment with the oxidizing mixture, always drying the paper after addition until the iodine colour is no longer visible. Now add 1 drop of 1% alcoholic solution of fluorescein and warm the paper by placing it on a watch glass covering a beaker containing boiling water. A red ring or a stain develops if bromide is present.

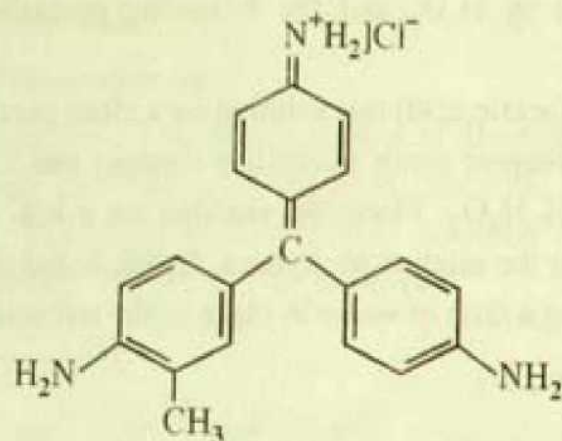
Limit of identification : 0.3γ of Br_2

Limit of dilution : 1:1.6×10⁵.

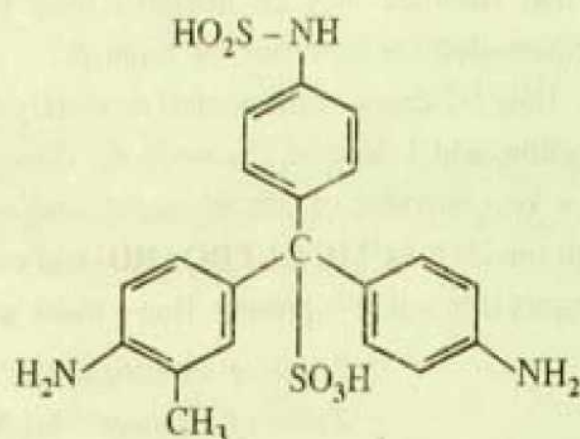
(2) Fuchsin (Maganta) test

Reagent : 0.1% solution of fuchsin just decolourized by sodium bisulfite solution.

The basic triphenylmethane dye stuff, fuchsin, is rose-red (maganta) coloured due to the quinoidal structure (1) of its cation. The dye is decolourised by neutral solution of bisulfite to a colourless product, N-sulfinic acid of *p*-fuchsin-leuco-sulfonic acid (2). Bromine converts this colourless dye stuff into a blue or violet coloured brominated dye stuff. Neither chlorine nor iodine can affect the colourless fuchsin bisulfite compound (2). Hence this reaction is most suitable for detection of bromide in presence of chloride and iodide.



(1)
rose-red



(2)
colourless

Place 1-2 drops of the neutral or weakly acidic test solution (or a small amount (<0.1g) of the powdered sample) in a semi-micro reaction tube fitted with a dropper with the aid of a rubber cork. Add 2-4 drops of 25% chromic acid solution and hang a drop of the reagent solution at the capillary head of the dropper and close the reaction tube with the stopper (Fig. 3.29b). Warm the contents gently (don't boil) for a few minutes. After a short period, the reagent drop in the capillary head assumes a violet colour.

Limit of identification: 3γ of Br⁻

Limit of dilution: 1 : 5 × 10⁴

5.13 Reactions of Iodide (I⁻)

Iodides of silver, mercury (I), mercury (II), copper (I) are sparingly soluble. Iodides of most other metals are soluble like the chlorides and the bromides.

Indication

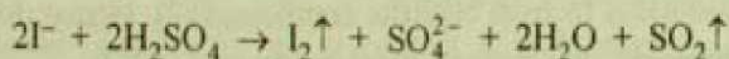
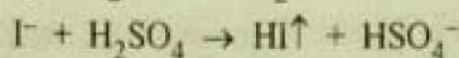
CAUTION : All dry tests involving evolution of iodine vapour should be carried out inside a **FUME CUPBOARD**.

(1) Dry test tube heating

Some iodides decompose on heating, violet vapour of iodine appears, which deposits as violet to black crystals on the cooler part of the test tube (sublimate).

(2) Concentrated sulfuric acid

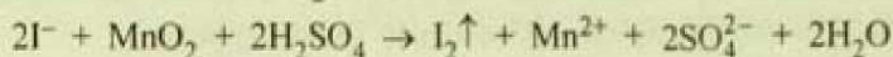
When iodide salts are heated with conc. H₂SO₄, violet vapour of I₂ appears as H₂SO₄ oxidizes iodide to iodine. Some hydrogen iodide is also formed. Sulfuric acid is reduced to various products, eg. SO₂, S and H₂S :



Place a small amount ($<0.1\text{g}$) of the dry sample in a semi-micro test tube, add 1-2 drops of conc. H_2SO_4 . Plug the test tube with a piece of clean cotton wool (Fig. 3.27a). Heat the mixture gently. Violet vapour appears if iodide is present.

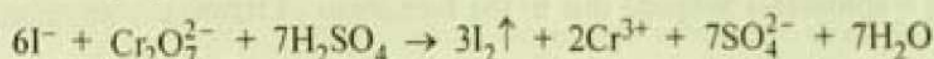
(2) Concentrated sulfuric acid + MnO_2

Mix a small amount ($<0.1\text{g}$) of the sample with equal amount of manganese dioxide and 1-2 drops of conc. H_2SO_4 in a semi-micro test tube. Plug the test tube with a piece of clean cotton wool (Fig. 3.27a) and heat the mixture gently. Dense violet vapour of I_2 appears as MnO_2 oxidizes iodide to set free I_2 and itself is reduced to colourless Mn(II) salt.



(3) Concentrated H_2SO_4 + $\text{K}_2\text{Cr}_2\text{O}_7$

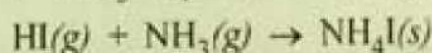
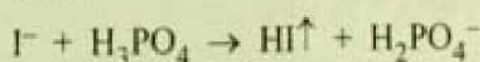
In presence of sulfuric acid, dichromate oxidizes iodide to set free iodine and itself is reduced to green Cr(III) sulfate.



Mix a small amount ($<0.1\text{g}$) of the sample with equal amount of $\text{K}_2\text{Cr}_2\text{O}_7$ and 1-2 drops of conc. H_2SO_4 in a semi-micro test tube. Plug the test tube with a piece of clean cotton wool (Fig. 3.27c) and heat gently. Violet vapor of I_2 appears. Hold a drop of NaOH solution ($\sim 2M$) using a capillary dropper at the issuing gas, the drop does not become yellow (difference from chloride).

(4) Concentrated phosphoric acid

Place a small amount ($<0.1\text{g}$) of the sample and 1-2 drops of conc. H_3PO_4 in a semi-micro test tube. Plug the test tube with a piece of cotton wool (Fig. 3.27b) and heat gently. Colourless vapour of HI appears, which intensifies on contact with ammonia due the formation of ammonium iodide.



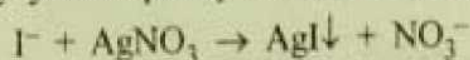
Reactions of Iodide ion in Solution

Tests with aqueous extract or neutralized Na_2CO_3 extract.

(1) Tests involving precipitation of iodide salts

(i) Silver nitrate solution

To 1 drop of neutral or weakly acidic (HNO_3) test solution add 1 drop of silver nitrate solution. Curdy yellow precipitate of silver iodide appears.



The precipitate of AgI is insoluble in dil. HNO_3 , dilute ammonia (distinction from chloride), concentrated ammonia (distinction from bromide), but readily soluble in concentrated solution of sodium thiosulfate, producing a clear solution, which gradually turns brown, finally black due to precipitation of Ag_2S . This transformation is accelerated on warming. (cf. Chloride tests).

(ii) Lead acetate solution

To 1-2 drops of the neutral or weakly acidic (acetic acid) test solution, add 1 drop of lead acetate solution. Yellow precipitate of lead iodide appears,



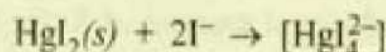
The yellow precipitate of lead iodide dissolves on boiling with water, forming a colourless solution and reappears as golden yellow plates (spangles) on cooling.

(iii) Mercuric chloride solution (POISON)

To 1 drop of the neutral or weakly acidic (HNO_3) test solution add 1 drop of mercuric chloride solution. Scarlet red precipitate of mercuric iodide appears.



Take a few particles of the precipitated HgI_2 in a semi-micro test tube and add a few more drops of the test solution. If iodide is present in the test solution, the red precipitate of HgI_2 dissolves, giving a colourless solution due to the formation of tetraiodomercurate (II) complex, $[\text{HgI}_4]^{2-}$ ion.



(2) Tests by oxidation of iodide to iodine (Confirmation)

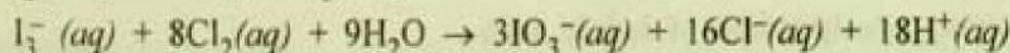
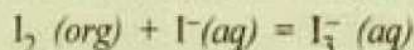
(a) Chlorine-water

[It is convenient to use a dilute solution of sodium hypochlorite acidified with dil. HCl].

Take 1-2 drops of the neutral or weakly acidic (acetic acid) test solution and 1 ml of chloroform in a semi-micro test tube. Add 1 drop of chlorine-water (or acidified hypochlorite solution) and shake. The organic layer at the bottom assumes a violet colour as iodine set free due to oxidation of iodide by chlorine, dissolves in CHCl_3 .



Add a few more drops of chlorine water and shake. The violet colour gradually disappears as iodine is further oxidized by Cl_2 to iodate.



(b) Potassium (or sodium) nitrite solution

Iodide in weakly acidic (acetic acid) solution is oxidized to iodine by nitrite ion (distinction from chloride and bromide) :



(i) Take 1-2 drops of the weakly acidic (dil. H_2SO_4 or acetic acid) test solution and 1 ml of chloroform in a semi-micro test tube, add a small crystal of sodium (or potassium) nitrite and shake. The chloroform layer assumes a violet colour.

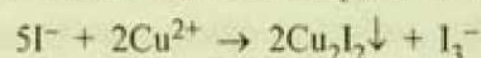
(ii) Place a drop of the test solution on a drop reaction paper, add 1 drop of dil. H_2SO_4 (or acetic acid) and dry. Add 1 drop of starch indicator and allow to dry. Now add a drop of 5% sodium or potassium nitrite solution. A blue colouration appears as iodine liberated from the reaction of iodide with nitrite, forms a blue adsorption product with starch indicator.

Limit of identification : 2.5γ of I_2

Limit of dilution : 1 : 2×10^4 .

(c) Copper sulfate solution

Although $E^\circ (\text{Cu}^{2+}/\text{Cu}^+)$, 0.15 volt is lower than $E^\circ (\text{I}_2/2\text{I}^-)$, 0.535 volt, but due to low solubility of CuI , or, Cu_2I_2 formal potential of $\text{Cu}^{2+}/\text{Cu}^+$ couple becomes sufficiently higher than that of $\text{I}_2/2\text{I}^-$ couple (cf. Sect. 2.4). As a result, Cu^{2+} ion oxidizes iodide ion to set free iodine with precipitation of Cu_2I_2 . Although Cu_2I_2 is white in colour, but the colour of the precipitate appears brown, due to adsorption of iodine (i.e. I_3^- ion).



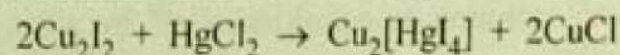
On addition of drops of sodium thiosulfate solution, the white colour of precipitated Cu_2I_2 is restored, as I_2 is reduced back to iodide by thiosulfate ($\text{S}_2\text{O}_3^{2-}$) ion, which is oxidized by I_2 to tetrathionate ($\text{S}_4\text{O}_6^{2-}$) ion.



If these reactions are carried out in presence of starch indicator which form a blue coloured adsorption product with iodine, a colour change from blue to white is observed on addition of thiosulfate solution.

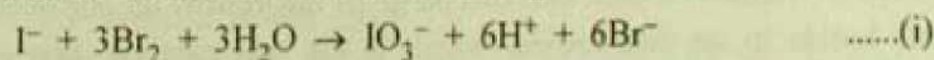
Place 1-2 drops of copper sulfate solution on a spot plate, add drops of dilute ammonia until a faint permanent turbidity appears, avoid excess NH_3 . Add a crystal of ammonium bifluoride and stir with a glass rod. The turbidity disappears. Add one drop of neutral or weakly acidic (acetic acid) test solution. A brown precipitate or turbidity appears, depending upon the amount of iodide ion present. Now add 1 drop of starch indicator solution. An intense blue colouration appears. Add a crystal of sodium thiosulfate and stir with a glass rod. The blue colour is discharged and the milk white colour of Cu_2I_2 precipitate becomes clearly visible.

Add a drop of mercuric chloride to the white slurry of Cu_2I_2 . The precipitate assumes a scarlet red colour due to the formation of Cu(I) tetraiodomercurate (II) complex.

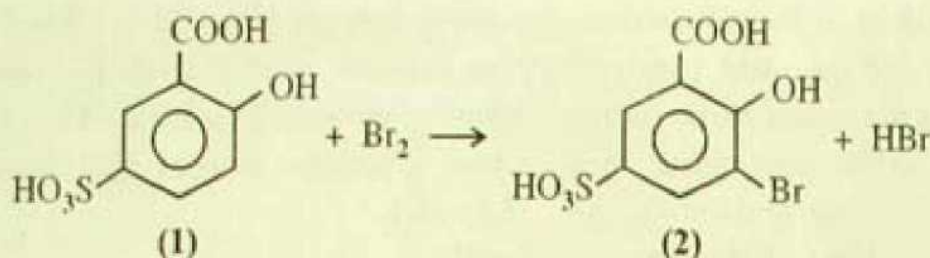


(3) Test by oxidation of iodide to iodate

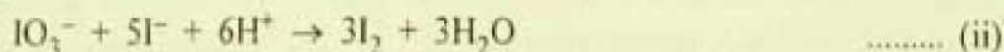
Iodide is oxidized to iodate in neutral solution by bromine water.



Unreacted bromine has to be removed before proceeding to test for the iodate that is produced. Removal of bromine is accomplished by adding sulfosalicylic acid (1) which consumes bromine to form colourless bromosulfosalicylic acid (2).



The resulting solution containing iodate ion on treatment with soluble iodide, liberates iodine, which may be detected by its characteristic tests.



Since one *mole* of iodide ion gives one *mole* of iodate ion (i) and one *mole* of iodate ion in turn liberates six mole of iodine atoms (ii), the sensitivity of the test is remarkably high and very small amount of iodide can be detected by this test. Chloride and bromide do not interfere. Oxyhalides interfere, as they oxidize iodide to iodine in acidic solution.

Reagents :

- (i) Bromine-water : 4% solution in water (**CAUTION**)
- (ii) Sulfosalicylic acid
- (iii) 5% solution of cadmium iodide (CdI_2) in 1% solution of cadmium sulfate in water.
- (iv) Starch indicator solution.

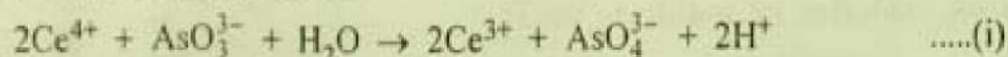
Place a drop of the neutral or weakly acidic test solution on a spot plate, add drops of bromine-water until a faint yellow colour persists due to excess bromine. Now add several small crystals of sulfosalicylic acid to consume the excess bromine and mix with a glass rod. Wait for 4-5 minutes and then blow air over the solution at intervals using a pipette or a dropper for thorough mixing and aeration to remove traces of bromine vapour that may remain in the air over the solution, [so that iodine is not liberated by the excess bromine on addition of iodide in the subsequent step]. Add a drop of cadmium iodide reagent mixed with a drop of starch indicator. A blue colouration is produced immediately on addition of starch- CdI_2 solution if iodide is present in the original test solution. Run a blank test.

Limit of identification : 0.05% of I_2

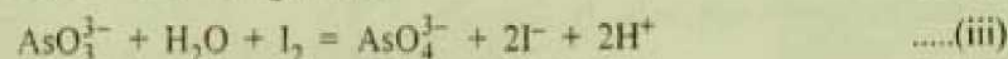
Limit of dilution : 1 : 1×10^6 .

(4) Catalytic acceleration of $\text{Ce}^{\text{IV}} + e \rightarrow \text{Ce}^{\text{III}}$ reduction by arsenite (POISON)

Reduction of yellow coloured Ce^{IV} solution to colourless Ce^{III} by arsenite (AsO_3^{3-}) ion in acidic solution is a very slow reaction,



But in presence of traces of iodide ion, discharge of the yellow colour occurs very quickly, as Ce^{4+} oxidizes iodide to set free iodine, which is the real catalyst, that oxidizes arsenite to arsenate and itself is reduced back to iodide (i.e. catalyst is regenerated),



The overall reaction (i) is arrived at by summing up the two step reaction (ii) and (iii). Although, in acid medium, the reaction (iii) tends to be left shifted, oxidation of As^{III} to As^{V} takes place in presence of Ce^{IV} , as iodide ions are constantly used up by reaction (ii), as a result of which the reaction (iii) remains right shifted.

Bromide, chloride, nitrate, sulfate interfere only in case of detection of very small amounts of iodide. A blank test should always be carried out. Coloured metal ions, eg, Fe^{III} , Ni^{II} , Cu^{II} , Co^{II} , UO_2^{2+} interfere. Mn^{II} , Ag^{I} , Hg^{I} ions, which reduce Ce^{IV} , impair the reaction. In such cases a more concentrated solution of Ce^{IV} should be used to overcome these difficulties. Barium, strontium, lead should be absent, since under the condition of this experiment, these are precipitated as sulfates which become yellow coloured due to coprecipitation of Ce^{IV} ions.

On two adjacent cavities of a spot plate place 1 drop of Ce^{IV} solution plus one drop of sodium arsenite solution. While the solutions are still yellow, add one drop of weakly acidic test solution in one of the cavities and a drop of dil. H_2SO_4 on the other. Rapid discharge of yellow colour in the cavity containing the test solutions indicates the presence of iodide.

Reagents:

- (i) Ce^{IV} solution : 0.05M ceric ammonium sulfate in 2N sulfuric acid.
- (ii) 0.1N sodium arsenite solution (made neutral or slightly acidic with dil. H_2SO_4).

Limit of identification : 0.05% of KI

Limit of dilution : 1 : 1×10^6 .

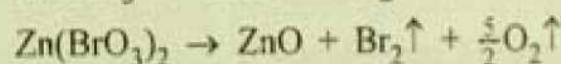
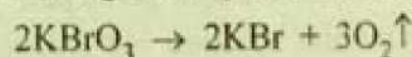
5.14. Reactions of Bromate (BrO_3^-)

Bromates of most metals are soluble in water except silver, mercury (I), lead, barium bromates, which are sparingly soluble.

Indication

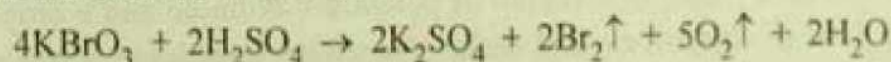
(1) Action of heat

Na, K, Ca bromates on heating decompose to bromides with evolution of oxygen. Transition metal bromates on heating decompose to oxides evolving oxygen and brown vapour of bromine.



(2) Concentrated sulfuric acid

Add 1-2 drops of conc. H_2SO_4 to a small amount (<0.1g) of the powdered sample in a semi-micro test tube, plug with a piece of clean cotton wool (Fig. 3.27a). O_2 gas and brown vapour of bromine are evolved in the cold.



Reactions of Bromate ion in solution

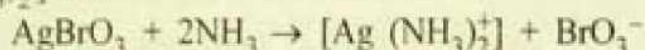
The following tests may be performed with aqueous extract or neutralized sodium carbonate extract of the sample.

(1) Silver nitrate solution

(a) To 1-2 drops of neutral or weakly acidic (dil. HNO_3) test solution add 1 drop of silver nitrate solution. White precipitate of silver bromate appears.



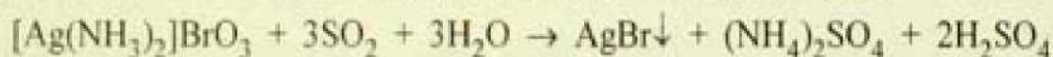
The precipitate is insoluble in dil. HNO_3 but soluble in hot water. It is also soluble in dilute ammonia solution (similarity with chloride, difference from bromide) forming the complex $[\text{Ag}(\text{NH}_3)_2]^+$ ion.



CAUTION : Discard the ammoniacal solution of silver nitrate immediately after test to avoid explosion (*cf.* chloride and bromide reactions).

(b) Reduction by SO_2 -water

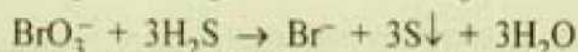
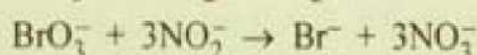
To the ammoniacal solution of silver bromate, obtained in test (1a) add a few drops of SO_2 -water, (or, sodium or potassium nitrite or H_2S -water). Pale yellow precipitate of silver bromide appears due to the reduction of bromate ion to bromide ion :



The precipitate of silver bromide is insoluble in dilute ammonia but soluble in concentrated ammonia (difference from iodate).

(2) SO_2 -water or bisulfite solution

SO_2 -water (or bisulfite HSO_3^- ion) reduces bromate to bromide in weakly acidic or neutral solution. H_2S and nitrite ion also reduce bromate to bromide :

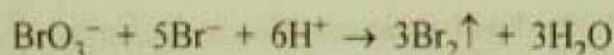


The resulting solution on treatment with silver nitrate solution, gives pale yellow precipitate of silver bromide, which is insoluble in dilute ammonia solution but soluble in concentrated ammonia (distinction from iodate).

CAUTION : Discard the ammoniacal solution of silver salt immediately after the test to avoid explosion.

(3) Hydrobromic acid or Potassium bromide

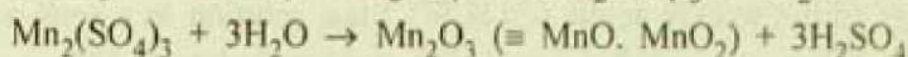
In a semi-micro test tube, mix 1-2 drops of the neutral or weakly acidic test solution, 1 drop of hydrobromic acid (HBr) or a crystal of potassium bromide and a drop of dilute sulfuric acid ($\sim 2N$). Add 1 ml of chloroform and shake. The chloroform layer assumes a yellow brown colour, due to bromine set free as a result of oxidation of bromide ion by bromate ion in acid medium.



Confirmation

(1) Manganous sulfate-Benzidine test

When a bromate salt is warmed with a solution of manganous sulfate in presence of dilute sulfuric acid ($\sim 2N$), bromate oxidizes Mn (II) to Mn(III) and a red colouration is initially formed. On boiling the mixture or better on adding alkali acetate, a brown precipitate of hydrated Mn(III) oxide is formed, which when treated with a solution of benzidine in acetic acid, oxidizes benzidine to benzidine blue. (*cf.* silicate, fluoride tests).



Place 1 drop of the neutral or weakly acidic (dil. H_2SO_4) test solution in a semi-micro test tube, add 1 drop of 2% manganous sulfate solution acidified with dilute sulfuric acid ($\sim 2N$) and digest the mixture for 2-3 minutes on a hot water bath. Cool to room temperature. Add 1 drop of 0.05% solution of benzidine in 1 : 10 acetic acid and a few crystals of sodium acetate. A blue colouration indicates the presence of bromate in the sample.

Chlorate, iodate do not give red colouration or a precipitate under the same condition and do not interfere.

Limit of identification : 20% of KBrO_3

Limit of dilution : 1 : 2500.

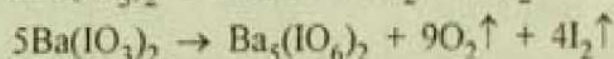
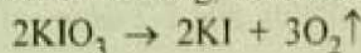
5.15 Reactions of Iodate (IO_3^-)

Alkali metal iodates are soluble in water. Iodates of other metals are not only sparingly soluble, but also less soluble than the corresponding bromates and chlorates.

Indication

(1) Action of heat

Iodates of all metals are decomposed on heating and oxygen evolution is their common feature. In addition to O_2 evolution, alkali metal iodates are transformed to iodides. Iodates of most bivalent metals on heating produce metallic oxides and violet vapour of iodine, except barium iodate, which on heating, is transformed to paraperiodate, with evolution of O_2 and I_2 .

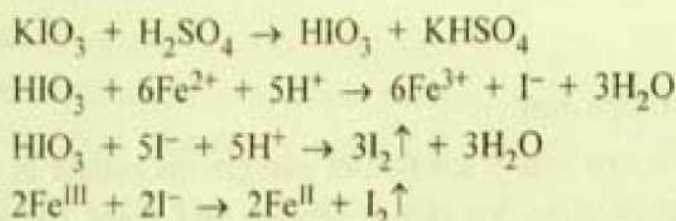


(2) Hot concentrated sulfuric acid

No action in absence of any reducing agent.

(3) Hot concentrated H_2SO_4 + Reducing agent (eg, FeSO_4)

Iodate is initially reduced to iodide and Fe^{II} is oxidized to Fe^{III} . Violet vapour of iodine appears due to oxidation of iodide by unreacted iodate and also by Fe^{III} produced.

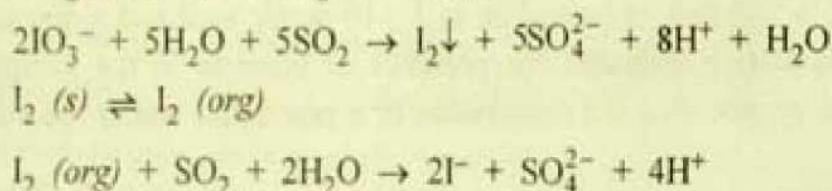


Reactions of Iodate ion in solution

The following tests should be carried out with the aqueous extract or neutralized Na_2CO_3 extract of the sample.

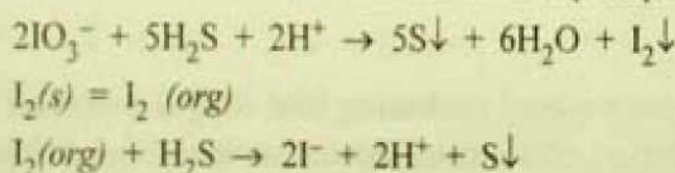
(1) SO_2 -water

Place 1-2 drops of the weakly acidic (dil. H_2SO_4) test solution in a semi-micro test tube, add a few drops of SO_2 -water and shake well. SO_2 reduces iodate to iodine, which forms a brown precipitate. Add 1 ml of chloroform and shake well, the chloroform layer assumes a violet colour. Add a few more drops of SO_2 -water, and shake. Violet colour of the organic layer disappears as SO_2 -water reduces I_2 to iodide.



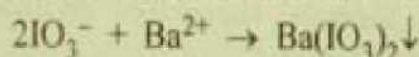
(2) H_2S -water

To 1-2 drops of the weakly acidic (dil. H_2SO_4) test solution add a few drops of H_2S -water. Brown precipitate of iodine appears due to reduction of iodate by H_2S . Add 1 ml of chloroform and shake. Iodine dissolves in chloroform forming a violet coloured organic layer. Add a few more drops of H_2S -water and shake. The violet colour gradually disappears as H_2S reduces I_2 to iodide and itself is oxidized to elemental sulfur that precipitates :



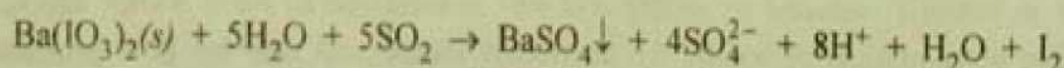
(3) Barium chloride solution

To 1-2 drops of the weakly acidic (dil. HCl) test solution add 1-2 drops of barium chloride. White precipitate of barium iodate is formed.



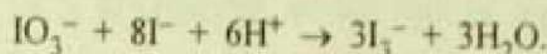
The precipitate is sparingly soluble in hot water and in dilute HNO_3 , but insoluble in ethanol (difference from iodide).

Add a few drops of SO_2 -water and 1 ml of chloroform to the precipitate and shake. The chloroform layer assumes a violet colour as iodine is set free due to reduction of IO_3^- ion by SO_2 -water.



(4) Potassium iodide solution

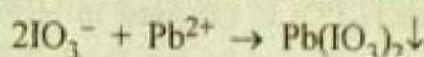
In a semi-micro test tube mix 1-2 crystals of potassium iodide and 1-2 drops of the neutral iodate solution and a drop of starch indicator. The mixture remains colourless. Now acidify the mixture with either dil. HCl or acetic acid or tartaric acid. The mixture assumes a blue colour as iodine is liberated from reaction of iodate with iodide in weakly acidic medium.



Alternatively, mix 1-2 crystals of KI, 1-2 drops of the neutral test solution and 1 ml of chloroform. Now add a few drops dil. HCl (or H_2SO_4) until acidic and shake. The chloroform layer assumes a violet colour due to dissolution of I_2 liberated by the reaction of IO_3^- with I^- .

(5) Lead acetate

To 1-2 drops of the weakly acidic (dil. acetic acid) test solution, add 1 drop of lead acetate solution. White precipitate of lead iodate is formed.



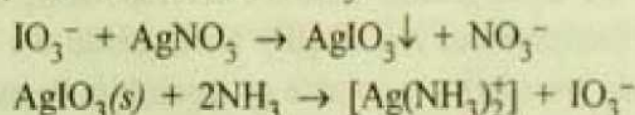
(6) Mercuric nitrate solution (POISON)

To 1-2 drops of weakly acidic test solution add 1 drop of mercuric nitrate. White precipitate of mercury (II) iodate is formed (difference from ClO_3^- and BrO_3^-).

Note : Mercury (II) chloride, being covalent, remains practically unionized, consequently it does not form any precipitate with iodate.

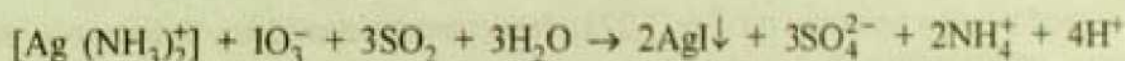
(7) Silver nitrate solution

To 1-2 drops of the weakly acidic [dil. HNO_3] test solution add 1 drop of silver nitrate solution. A curdy white precipitate of silver iodate is formed, which is readily soluble in dil. NH_3 , but sparingly soluble in dil. HNO_3 ,



CAUTION : Discard the ammoniacal solution of silver salt immediately after the test to avoid explosion.

To the ammoniacal solution of AgIO_3 add a few drops of SO_2 -water. Yellow precipitate of silver iodide appears, as IO_3^- is reduced to I^- by SO_2 -water.

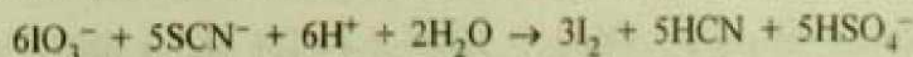


The precipitate of AgI is insoluble even in concentrated NH_3 solution.

Confirmation

(1) Test with potassium (or ammonium) thiocyanate (CAUTION)

In acidic medium, iodate is reduced to iodine by thiocyanate, which is oxidized to sulfate:



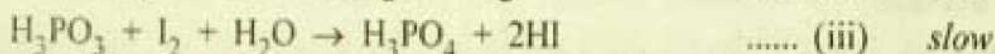
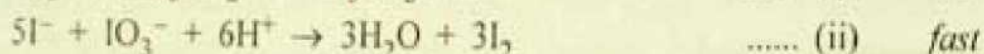
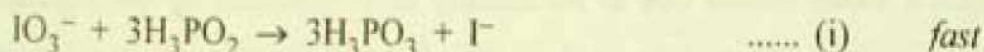
Place a drop of 5% solution of potassium (or ammonium) thiocyanate on a starch paper and then add a drop of acidified test solution. A blue stain indicates the presence of iodate in the sample.

Limit of identification : 4γ of NaIO_3

Limit of dilution : 1 : 1.2×10^4 .

(2) Test with hypophosphorous acid

Hypophosphorous acid (H_3PO_2) reduces iodate to iodide and itself is oxidized to phosphoric acid (H_3PO_4) even in the cold. The redox reaction takes place in three distinct steps differing in speeds :



As the reduction of IO_3^- to I^- (i) and subsequent oxidation of I^- by unreacted IO_3^- to I_2 (ii) are rapid but the last reaction (iii) in which H_3PO_3 is oxidised to H_3PO_4 by I_2 is a slow process, the intermediate production of I_2 may be revealed by the formation of transient blue colour of starch-iodine complex, and this offers a means of detection iodate. Bromate, chlorate do not interfere.

Place a drop of the neutral test solution on a spot plate, add 1 drop of starch indicator solution and then a drop of dilute solution of hypophosphorous acid. Appearance of a transitory blue colouration indicates the presence of iodate in the test solution.

Limit of identification : 1γ of HIO_3

Limit of dilution : 1 : 5×10^4 .

5.16 Reactions of Ferricyanide [Hexacyanoferrate (III)], $[\text{Fe}(\text{CN})_6]^{3-}$

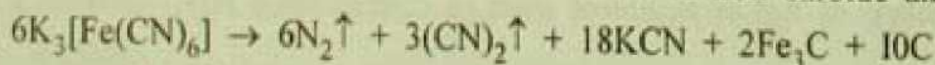
Ferricyanide salts in general are more soluble than the corresponding ferrocyanide salts. Alkali and alkaline earth metal ferricyanides and Fe(III) ferricyanide are soluble in water. Ferricyanides of most other metals are sparingly soluble or insoluble. Insoluble ferricyanides are decomposed by alkali to form alkali ferricyanide and hydrated metallic oxides.

Indication

(1) Orange yellow colour in solid state and in solution.

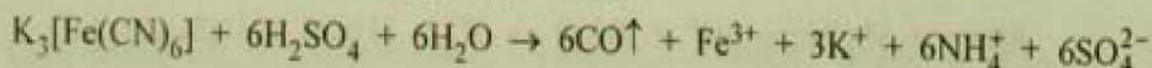
(2) **Ignition test** [CAUTION, must be done in **FUME CUPBOARD**].

When heated in a dry test tube (*cf.* Fig. 3.27a), ferricyanides completely decompose, evolving N_2 and $(\text{CN})_2$ (POISON) gases and leave a black residue of iron carbide and carbon.



(3) **Hot concentrated sulfuric acid** (CAUTION : Must be done in **FUME CUPBOARD**)

On heating with conc. H_2SO_4 , ferricyanides decompose completely with evolution of CO gas which burns with blue flame (*cf.* Fig. 3.30a).



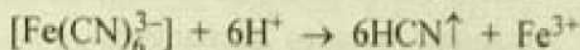


Reactions of Ferricyanide Ion in Solution

Aqueous extract or neutralized Na_2CO_3 extract of the sample should be used for the tests,

(1) Dilute sulfuric acid

Dilute sulfuric acid has no reaction in the cold, but on boiling (*cf.* Fig. 3.31) [CAUTION: Must be done in **FUME CUPBOARD**] ferricyanides decompose to set free Fe^{3+} ion in solution with evolution of HCN (POISON), which may be absorbed in NaOH solution.



(2) Concentrated hydrochloric Acid

When a saturated solution of a ferricyanide salt is treated with conc. HCl in the cold, brown precipitate of the free hexacyanoferric acid or ferricyanic acid, $\text{H}_3[\text{Fe}(\text{CN})_6]$, appears:



(3) Silver nitrate solution

Place 1 drop of the neutral or weakly acidic test solution on two adjacent cavities a spot plate and add 1 drop of silver nitrate solution to each cavity. Orange red precipitate of silver ferricyanide appears



Add a few drops of dilute ammonia solution to one of the cavities, the precipitate dissolves due to the formation of the complex $[\text{Ag}(\text{NH}_3)_2]^+$ ion.

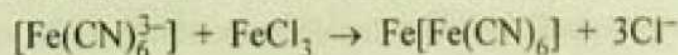


CAUTION : Discard the ammoniacal solution of $[\text{Ag}(\text{NH}_3)_2]^+$ immediately to avoid explosion.

Add a few drops of dil. HNO_3 to the other cavity, the precipitate remains undissolved.

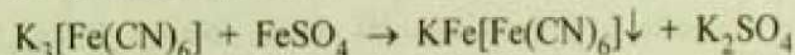
(4) Ferric chloride solution

To 1 drop of weakly acidic test solution on a spot plate add 1 drop of ferric chloride solution. A brown colouration appears due to the formation of ferric ferricyanide (*cf.* tests for Fe^{III}).



(5) Ferrous sulfate solution

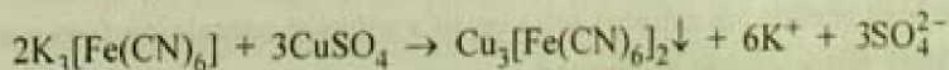
To a drop of the neutral or weakly acidic test solution on a spot plate add 1 drop of ferrous sulfate or Mohr's salt solution in dil. H_2SO_4 (2*N*). An intense blue precipitate of (*Prussian blue*) appears if ferricyanide is present,



The composition of the blue precipitate may be $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]$ (*Turnbull's blue*) or $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ (*Prussian blue*) or both (*cf.* reactions of Fe^{II} , Fe^{III}).

(6) Copper sulfate solution

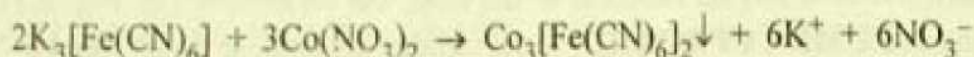
To 1 drop of the neutral or weakly acidic test solution on a spot plate add 1 drop of dilute copper sulfate solution ($\sim 0.1\text{M}$). Green precipitate of cupric ferricyanide appears.



Add drops of HCl to the green precipitate. The precipitate does not dissolve.

(7) Cobalt nitrate solution

In two adjacent cavities of a spot plate take 1 drop of the weakly acidic test solution, add 1 drop of cobalt nitrate solution to both the cavities. Red precipitate of cobalt (II) ferricyanide appears.



Add drops of ammonia solution to one of the cavities, the precipitate dissolves. Add drops of dil. HCl to the other cavity, the precipitate remains unchanged.

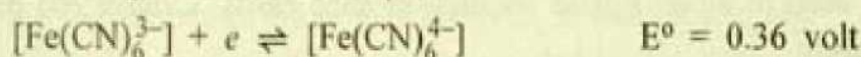
Confirmation

(1) Benzidine blue test

Reagents :

- (i) Saturated solution of benzidine in 2M acetic acid,
- (ii) 10% KI solution in water.

The ferricyanide-ferrocyanide redox couple,



does not normally oxidize benzidine. Even in a solution of pure ferricyanide, very trace amount ferrocyanide is always present in equilibrium and vice-versa. So, if by addition of a suitable reagent, ferrocyanide is removed from the redox equilibrium, the E^0 value of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ couple will increase and may attain such a value that ferricyanide can oxidize (i) benzidine to benzidine blue and (ii) iodide to I_2 (or I_3^-) which forms a blue colouration with starch indicator (*cf.* Sect 2.4j).

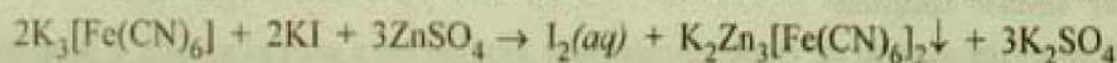
Ferrocyanide may be eliminated from the $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ redox equilibrium by several ways :

- (i) By lowering pH of the solution (*cf.* p-135) :

On addition of a strong acid such as hydrochloric acid, both the complex ions, $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ are protonated to form the corresponding acids, viz., $H_3[Fe^{III}(CN)_6]$ and $H_4[Fe^{II}(CN)_6]$, of which the latter acid has much lower degree of ionization. As a result, ferrocyanide ions are eliminated from the above redox equilibrium and consequently the formal potential of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ is increased.

- (ii) By addition of Zn (II) salt (*cf.* p.161) :

$[Fe(CN)_6]^{3-}$ does not liberate I_2 from potassium iodide solution [$E^0 (I_2/2I^-) = 0.53 \text{ volt}$]. But in presence of Zn^{2+} ions, sparingly soluble Zn(II) ferrocyanide (more appropriately, potassium zinc ferrocyanide) is precipitated out. As a result, $[Fe(CN)_6]^{3-}$ ion oxidizes iodide to iodine, which may be detected by blue colouration of starch indicator solution.



- (iii) By addition of lead acetate or lead nitrate solution :

On addition lead acetate (or nitrate) solution to a solution containing ferricyanide ion, white precipitate of lead ferrocyanide is formed,



Due to the precipitation of lead ferrocyanide, $[\text{Fe}(\text{CN})_6]^{3-}$ can oxidize (i) benzidine to benzidine blue and (ii) iodide to iodine.

(i) Mix 1 drop of the test solution, a crystal of potassium iodide plus a drop of starch indicator in three adjacent cavities of a spot plate. No blue colouration should be observed. Now add a drop of (1:1) HCl solution in one of the cavities. Blue colouration appears if ferricyanide is present.

(ii) Add a small crystal of zinc sulfate or zinc acetate to the second cavity and stir with a glass rod. Blue colouration appears if ferricyanide is present.

(iii) Add a drop of lead acetate solution to the third cavity and stir with a glass rod. Blue colouration indicates ferricyanide.

(iv) Mix a drop of the neutral or weakly acidic (acetic acid) test solution and a drop of benzidine reagent on a spot plate. Add 1 drop of lead acetate (or nitrate) or one drop zinc acetate (or sulfate) to precipitate ferrocyanide. Finally add 1 drop of sodium acetate. A blue precipitate or colouration indicates ferricyanide.

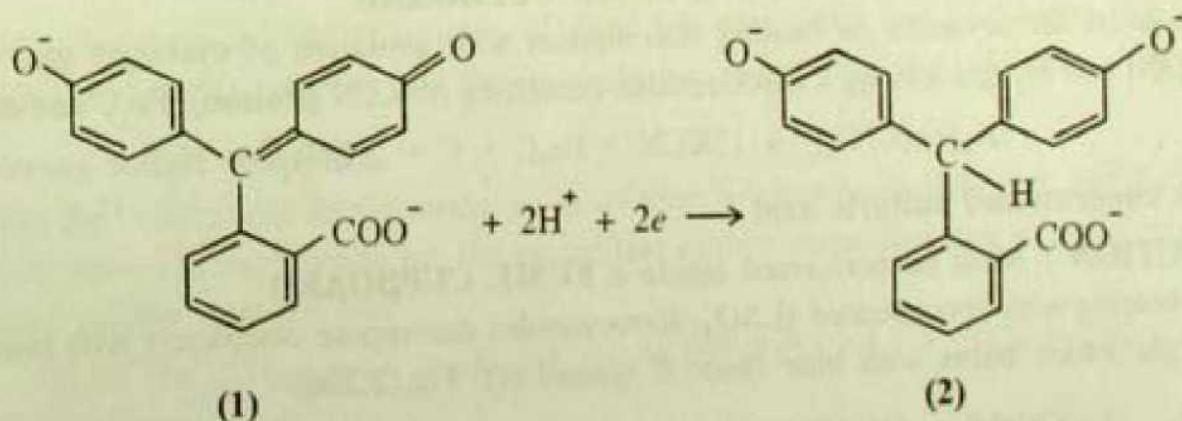
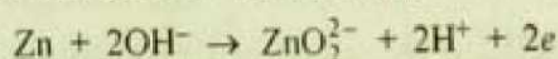
Limit of identification : 1γ of $\text{K}_3[\text{Fe}(\text{CN})_6]$

Limit of dilution : 1 : 5×10^4 (1 : 1×10^4).

In presence of 1000 times of $\text{K}_4[\text{Fe}(\text{CN})_6]$, the value are 5γ and 1 : 1×10^4 respectively.

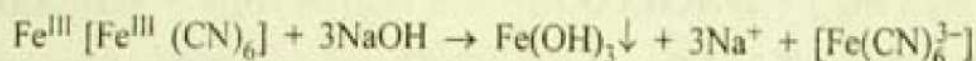
(2) Test with phenolphthalin

Alkaline solution of phenolphthalin (1) is red coloured. When warmed with Zn-dust, red alkaline solution of phenolphthalin becomes colourless due to the reduction of the quinoidal structure (1) to the benzenoidal structure (2).

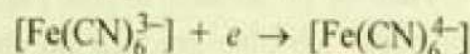


The red colour of phenolphthalin may be restored by oxidation. Colourless solution of reduced phenolphthalin on exposure to air gradually becomes red due to aerial oxidation. On addition of strong oxidizing agent, however, an intense red colour develops immediately. Alkali ferricyanides instantly oxidize colourless reduced alkaline phenolphthalin (2) to red coloured

quinoidal phenolphthalin (1). Alkaline solution of reduced phenolphthalin decomposes even insoluble ferricyanides, setting free alkali ferricyanides and precipitating metallic hydroxides or hydrous oxides.



$[\text{Fe}(\text{CN})_6]^{3-}$ ion set free, oxidizes colourless reduced phenolphthalin (2) to red coloured phenolphthalin solution (1) and itself is reduced to ferrocyanide $[\text{Fe}(\text{CN})_6]^{4-}$, according to



If a neutral or weakly acidic solution of ferricyanide is treated with Zn^{II} sulfate, white precipitate of zinc ferricyanide appears. If the precipitate after washing is treated with colourless alkaline phenolphthalin, the solution assumes an intense red colour.

Take 1 ml of dilute NaOH (1M) solution in a semi-micro test tube, add 1 drop of phenolphthalin indicator and a pinch of zinc dust. Warm slightly on a hot water bath until the red colour of phenolphthalin is discharged. Centrifuge and discard the residue. Place one drop of this colourless solution on a spot plate, add a few drops of the neutral or weakly acidic test solution. A red-pink colour develops if ferricyanide is present.

Note : This test of ferricyanide may be applied in presence of other oxidizing agents.

Limit of identification : 0.5γ of $\text{K}_3[\text{Fe}(\text{CN})_6]$

Limit of dilution : 1 : 1×10^5 .

5.17. Reactions of Ferrocyanide (Hexacyanoferrate (II)) : $[\text{Fe}(\text{CN})_6]^{4-}$

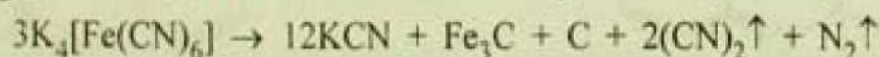
Alkali metal ferrocyanides are soluble in water. Ferrocyanides of other metals are either sparingly soluble or insoluble in water or in cold dilute acids. Insoluble ferrocyanides are decomposed by alkalies.

Indication

(1) Action of heat

CAUTION : Must be performed in **FUME CUPBOARD**

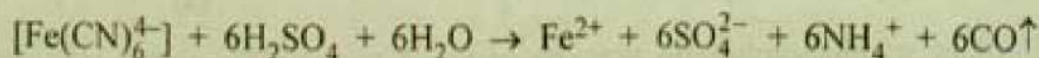
Potassium ferrocyanide on heating decomposes with evolution of cyanogen gas, $(\text{CN})_2$ [POISON] and N_2 gas leaving a black residue consisting of KCN (Poison), Fe_3C and carbon.



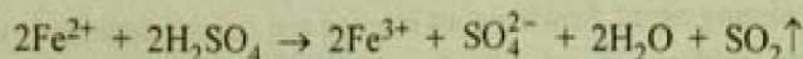
(2) Hot concentrated sulfuric acid

CAUTION : Must be performed inside a **FUME CUPBOARD**

On heating with concentrated H_2SO_4 , ferrocyanides decompose completely with evolution of CO gas which burns with blue flame if ignited (cf. Fig. 3.30a)



Small amount of SO_2 may also be formed due to reduction of H_2SO_4 by Fe^{2+} .

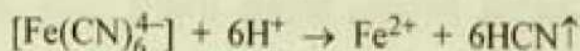




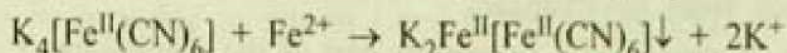
Reactions of Ferrocyanide Ion in Solution

(1) Dilute sulfuric acid

CAUTION: Must be carried out in **FUME CUPBOARD** having good ventilation. Ferrocyanide does not react with dilute H_2SO_4 in the cold. But on warming with dil. H_2SO_4 , ferrocyanide decomposes completely, producing hydrogen cyanide gas [**POISON**] (cf. Fig. 3.31b).



Fe^{2+} produced in this reaction combines with unreacted $[\text{Fe}(\text{CN})_6]^{4-}$ ion, producing initially a white precipitate of potassium iron (II) hexacyanoferrate (II) or potassium ferrous ferrocyanide.

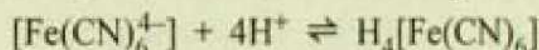


On exposure to air, the precipitate is gradually oxidized by oxygen of the air and ultimately soluble Prussian blue, potassium ferricferrocyanide, $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$, is produced :



(2) Hydrochloric acid

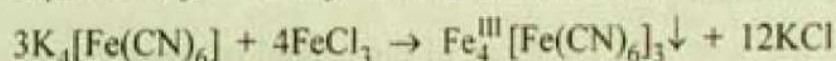
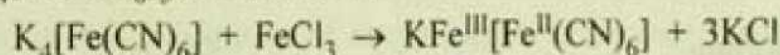
On treatment with (1:1) hydrochloric acid, weakly ionized ferrocyanic acid, $\text{H}_4[\text{Fe}(\text{CN})_6]$ is produced, which may be extracted into diethylether.



Ferrocyanic acid may be obtained in crystalline form on evaporation of the etherial layer.

(3) Ferric chloride solution

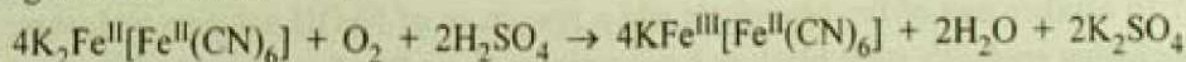
Take 1 drop of the neutral or weakly acidic test solution in a semi-micro test tube, add a drop of ferric chloride solution. Both soluble Prussian blue, $\text{KFe}[\text{Fe}(\text{CN})_6]$ and insoluble Prussian blue, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ are produced.



Add a few drops of NaOH solution (2M) to this precipitate and heat to boiling. Brown precipitate of $\text{Fe}(\text{OH})_3$ appears and ferrocyanide ion passes into the solution.

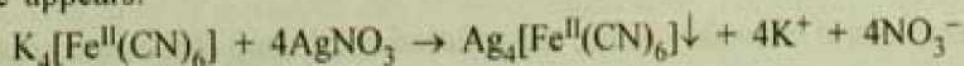
(4) Ferrous sulfate solution

When Fe^{2+} reacts with ferrocyanide ion in solution, a white precipitate of $\text{K}_2\text{Fe}^{\text{II}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ readily appears. On exposure to air, the precipitate rapidly turns blue due to aerial oxidation, producing soluble Prussian blue.



(5) Silver nitrate solution

In a semi-micro test tube, take to 1-2 drops of the neutral or weakly acidic (HNO_3) test solution and add 1-2 drops of silver nitrate solution (0.1 M). White precipitate of silver ferrocyanide appears.



Centrifuge the precipitate wash with water, discard the centrifugate, divide the precipitate into three parts and perform the following tests :

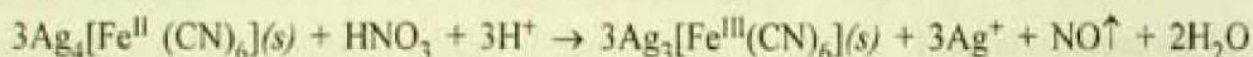
(i) To one part of the precipitate add a few drops of concentrated solution of sodium thiosulfate. The precipitate passes into solution, due to the formation of silver thiosulfato complex,



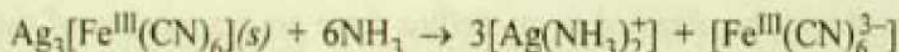
The solution gradually becomes turbid, forming brown, finally black precipitate of Ag_2S (cf. $\text{S}_2\text{O}_3^{2-}$ test).

(ii) Add a few drops of ammonia to another part of the precipitate, the precipitate does not dissolve (distinction from ferricyanide).

(iii) Add one drop of conc. HNO_3 to another part of the precipitate. The precipitate does not dissolve. Warm the mixture gently. The colour of the precipitate changes from white to orange red as HNO_3 oxidizes the precipitated silver ferrocyanide to the corresponding ferricyanide.



Cool and add a few drops of ammonia solution to render the mixture ammoniacal. The orange red precipitate of silver ferricyanide passes into solution due to the formation of diammine silver complex, $[\text{Ag}(\text{NH}_3)_2]^+$ ion,



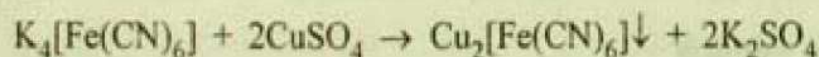
CAUTION : Discard the ammoniacal solution of $[\text{Ag}(\text{NH}_3)_2]^+$ immediately after test to avoid serious explosion due to the formation of Ag_3N (*fulminating silver*).

Limit of identification : 1γ of $[\text{Fe}(\text{CN})_6]^{4-}$

Limit of dilution : 1 : 4×10^5 .

(6) Copper sulfate solution

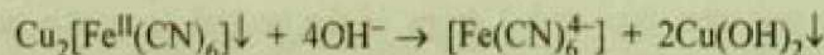
In a semi-micro test tube take 1-2 drops of the neutral or weakly acidic test solution and add 1-2 drops of copper sulfate solution (0.25M). Chocolate brown precipitate of copper (II) ferrocyanide appears.



Centrifuge, wash the precipitate with water and discard the centrifugate. Divide the residue into two parts and perform the following tests :

(i) To one part of the precipitate add acetic acid. The precipitate remains undissolved.

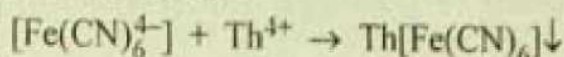
(ii) To another part of the precipitate add a few drops of NaOH solution and warm gently. The precipitate gradually turns black as it decomposes to set free ferrocyanide with precipitation of copper hydroxide :



(7) Thorium nitrate solution

To 1 drop of the neutral or weakly acidic test solution add 1 drop of thorium nitrate solution.

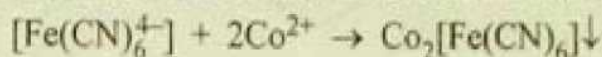
Colloidal white precipitate of thorium ferrocyanide appears (distinction from ferricyanide and thiocyanate, which do not react) :



The precipitate remains colloidal, does not settle and it is difficult to filter or centrifuge.

(8) Cobalt nitrate solution

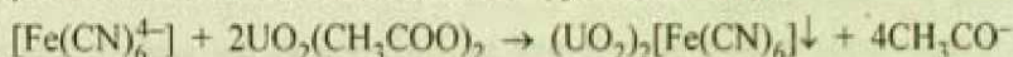
To a drop of the neutral or weakly acidic test solution add 2-3 drops of cobalt (II) nitrate solution (0.5M). Greyish green precipitate of cobalt (II) ferrocyanide appears.



The precipitate is insoluble in dil. HCl and dilute acetic acid.

(9) Uranyl acetate solution

Place a drop of the neutral or weakly acidic (acetic acid) test solution on a spot plate and add a drop of uranyl acetate (0.1M) and stir with a glass rod. A brown precipitate of uranyl ferrocyanide appears within two to three minutes (*cf.* Sect. 8.10) :



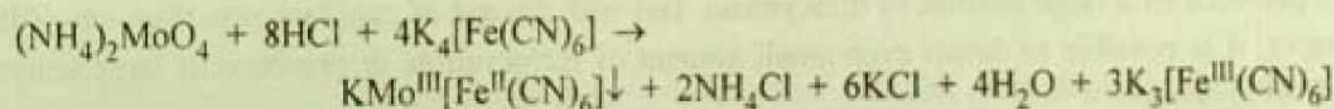
Limit of identification : 1γ of $\text{K}_4[\text{Fe}(\text{CN})_6]$

Limit of dilution : 1 : 5×10^4 .

Note : Ferricyanides react only in concentrated solution, and produce dirty yellow precipitate on long standing or on warming. These tests should be carried out on spot plate, but not on drop reaction paper, which is oxidized by ferricyanides.

(10) Ammonium molybdate in dilute hydrochloric acid

To 1 drop of the weakly acidic (dil.HCl) test solution on a spot plate, add 1 drop of ammonium molybdate reagent. Brown precipitate of molybdenum ferrocyanide appears (distinction from ferricyanide and thiocyanate) (*cf.* Sect. 8.8). Stoichiometry of the reaction may be,



The precipitate is not soluble in dilute acids, but dissolves in alkali hydroxide solutions.

(1) Confirmation

(1) Mercuric nitrate-2,2'-bipyridine (or 1,10-phenanthroline) test

Reagents :

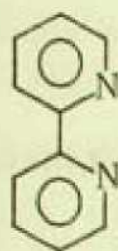
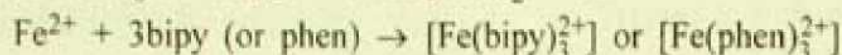
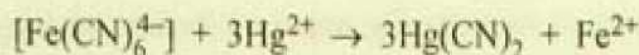
(i) 0.005M 2,2'-bipyridine (or 1,10-phenanthroline) in 0.01M HNO_3 ,

(ii) Mercuric nitrate 0.01M in 0.01M HNO_3 .

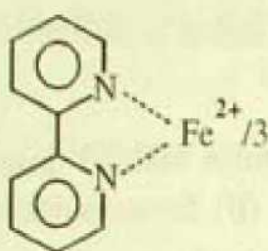
Ferrocyanides do not react with 2, 2'-bipyridine (bipy) (I) or 1, 10-phenanthroline (phen)

(2). But in presence of Hg^{2+} ions, ferrocyanide ion is decomposed to produce $\text{Hg}(\text{II})$ cyanide $\text{Hg}(\text{CN})_2$ or $[\text{Hg}(\text{CN})_4]^{2-}$ and Fe^{2+} ion is set free. If bipy or phen is present in the solution, intense red colouration is produced due to the formation of $[\text{Fe}(\text{bipy})_3]^{2+}$ (1a), or $[\text{Fe}(\text{phen})_3]^{2+}$

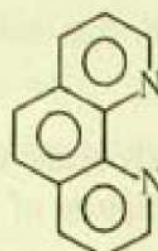
(2a) complex as the case may be :



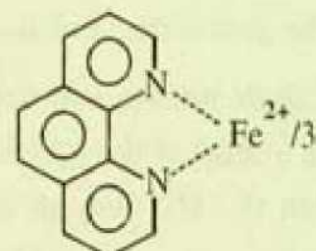
(1)



(1a)



(2)



(2a)

Take 1-2 drops of the neutral or weakly acidic test solution in a semi-micro test tube, add 5 drops of 2, 2'-bipyridine (or 1, 10-phenanthroline) reagent solution, 1 drop of mercuric nitrate solution (0.01M). Wait for some time or warm gently on a hot water bath. A red colouration soon develops if ferrocyanide is present. With increasing amount of Hg^{2+} ion, appearance of the red colour becomes faster.

Note : Ferricyanide is also decomposed by Hg^{2+} ion in the same manner, but Fe^{3+} ion set free does not interfere with the detection of ferrocyanide, as bipy (or phen) reacts only with Fe^{2+} ions.

Limit of identification : 0.2γ of $\text{K}_4[\text{Fe}(\text{CN})_6]$

Limit of dilution : 1 : 2.5×10^5 .

(2) Ferrocyanide is presence of thiocyanate by capillary separation

Thiocyanate reacts with ferric chloride solution producing intensely red coloured complex $[\text{Fe}(\text{SCN})_2]^{2+}$ ion, whereas, ferrocyanide reacts with ferric chloride to produce Prussian blue precipitate. The red colour of $[\text{Fe}(\text{SCN})_2]^{2+}$ complex is so intense that it often masks the blue colour of Prussian blue, particularly when a small amount of ferrocyanide has to be detected in presence of a large amount of thiocyanate. But with the aid of capillary separation on a filter paper, it is possible to detect even small amount of ferrocyanide in presence of large amount of thiocyanate.

(a) Impregnate a Whatman No. 1 filter paper strip with ferric chloride solution (0.5M) and allow the paper to dry. Add 1 drop of the weakly acidic test solution, a deep red spot is produced if thiocyanate is present. Allow the spot to dry. Now hold a solution of dil. (~1M) HCl on the spot with the aid of a capillary dropper or a capillary tube. A red coloured ring moves away from the central blue spot, if both thiocyanate and ferrocyanide are present.

Limit identification : 0.5γ of $[\text{Fe}(\text{CN})_6]^{4-}$ in presence of 5000 times of SCN^- ions.

Limit of dilution : 1 : 1×10^5 .

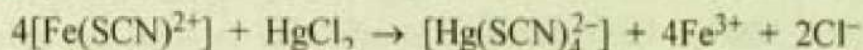
(b) Alternatively, place one drop of the weakly acidic test solution on three filter paper strips impregnated with ferric chloride solution (0.5M). Intense red spots are produced on all the three strips if thiocyanate is present. Now perform the following tests with the red spots.

(i) To one of the strips, add 1 drop ammonium bifluoride (or $\text{NH}_4\text{F}/\text{NaF}/(\text{KF})$ solution. The red colour is discharged as hard Fe^{3+} ion preferably binds hard F^- ion to form the colourless complex, $[\text{FeF}_6]^{3-}$ ion, leaving the soft SCN^- ion free.



The blue spot due to ferrocyanide now becomes visible.

(ii) Add a drop of mercuric chloride solution to the red spot on another filter paper strip. The red colour due to $[\text{Fe}(\text{SCN})^{2+}]$ is discharged as soft $\text{Hg}(\text{II})$ snatches the soft SCN^- ion from the hard-soft complex, $[\text{Fe}(\text{SCN})^{2+}]$, forming more stable soft-soft $[\text{Hg}(\text{SCN})_4]^{2-}$ complex ion which is colourless.



The blue spot due to Prussian blue now becomes visible.

Limit of identification : 0.5γ of $[\text{Fe}(\text{CN})_6]^{4-}$ in presence of 5000 times of SCN^- ion.

Limit of dilution : $1 : 1 \times 10^5$.

(iii) To the red spot on the third strip, add a drop of concentrated sodium thiosulfate solution. The red colour is discharged as thiosulfate reduce Fe^{III} in the $[\text{Fe}(\text{SCN})^{2+}]$ complex ions to set free Fe^{II} ions, which does not react with SCN^- . Thiosulfate has no effect on the Prussian blue precipitate, which now becomes visible.

If iodide is present, brown coloured iodine is liberated by Fe^{3+} along with the formation of intensely red coloured $[\text{Fe}(\text{SCN})^{2+}]$ complex and these together mask the Prussian blue colour due to ferrocyanide. However, this test 2(b) (iii) is applicable for testing ferrocyanide in presence of both iodide and thiocyanate.

Limit of identification : 0.5γ of $[\text{Fe}(\text{CN})_6]^{4-}$ in presence of 3000 times of SCN^- and

Limit of dilution : $1 : 1 \times 10^5$. 2000 times of I^- ions.

(3) Detection of ferrocyanide, ferricyanide and thiocyanate by capillary separation

Procedure - 1

Soak a Whatman No. 1 filter paper strip in a saturated solution of lead nitrate and allow the paper to dry in air. Add a drop of the test solution. If ferrocyanide is present, insoluble $\text{Pb}_2 [\text{Fe}(\text{CN})_6]$ is precipitated and gets fixed in the middle of the moist fleck. Ferricyanide and thiocyanate, if these ions are present, diffuse outward through the capillaries of the filter paper. Now add a drop of water with the help of a capillary tube at the middle of the fleck, the outer moist zone moves out faster. Allow the paper to dry. Now moisten one side of the spot with a drop of ferric chloride solution and the other side with a drop of freshly prepared ferrous sulfate (or Mohr's salt) solution. If Prussian blue fleck is formed at the centre, a Turnbull's blue and a blood red colouration of ferrithiocyanate appear at the borders.

Procedure-2

Impregnate a Whatman No. 1 filter paper strip with a drop of ferric chloride solution at the centre and add 1 drop of the test solution using a capillary tube. A dark coloured spot

appears. Dry the paper in air. Now hold a capillary dropper containing dilute (1:1) HCl solution at the centre of the spot in such a manner that the acid solution slowly tickles down and moisten the spot. As the wet zone moves out, three concentric circles appear. The blue spot of Prussian blue (due to ferrocyanide) remains fixed at the centre, a red ring of $[\text{Fe}(\text{SCN})^{2+}]$ on the outer boundary and a green ring (due to ferricyanide) remains in between.

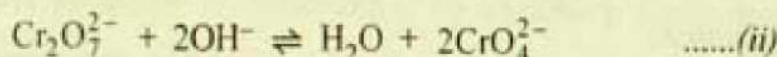
5.18 Reactions of Chromate (CrO_4^{2-}), Dichromate ($\text{Cr}_2\text{O}_7^{2-}$)

Chromates are yellow and dichromates are orange coloured. Alkali metal, ammonium, magnesium and calcium chromates and dichromates are soluble in water. Strontium chromate is sparingly soluble in water. Barium and lead chromates are insoluble in water. BaCrO_4 is soluble in mineral acid (HCl, HNO_3). Lead chromate is insoluble in acids but soluble in alkali due to amphoteric nature of lead oxide/hydroxide.

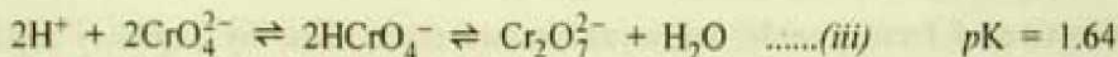
Dichromate and chromate are a conjugate acid-base pair. In presence of an acid i.e. H^+ ions, chromate ions are transformed to dichromate (i), whereas, in presence of a base, i.e. OH^- ions, dichromate ion is transformed to chromate (ii).



$$K = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{H}^+]^2[\text{CrO}_4^{2-}]^2} \quad \text{.....(ia)}$$



Bichromate, HCrO_4^- ion, is believed to be formed as an intermediate in reaction (i), which may be re-written as (iii),

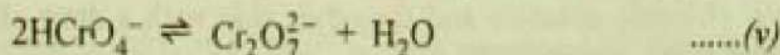


Bichromate ion ionizes as a weak acid,



$$K_1^H = \frac{[\text{H}^+][\text{CrO}_4^{2-}]}{[\text{HCrO}_4^-]} \quad \text{.....(iva)} \quad pK_1^H = 6.53$$

The bichromate-dichromate ion association equilibrium may be defined as,



$$K_2 = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{HCrO}_4^-]^2} \quad \text{.....(va)}$$

The ion association equilibrium constant (K)(ia), may be related to K_1^H and K_2 .

From equation (va),

$$\therefore [\text{Cr}_2\text{O}_7^{2-}] = K_2[\text{HCrO}_4^-]^2$$

From equation (iva),

$$\therefore [\text{CrO}_4^{2-}] = K_1^H[\text{HCrO}_4^-] / [\text{H}^+]$$

Substituting for $[\text{CrO}_4^{2-}]$ and $[\text{Cr}_2\text{O}_7^{2-}]$ in equation (ia) one obtains,

$$\therefore K = \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{CrO}_4^{2-}]^2[\text{H}^+]^2} = \frac{K_2[\text{HCrO}_4^-]^2[\text{H}^+]^2}{(K_1^H)^2[\text{HCrO}_4^-]^2[\text{H}^+]^2} = \frac{K_2}{(K_1^H)^2} \quad \text{..... (vi)}$$

$$\therefore \log K = 2pK_1^H - pK_2 \quad \text{..... (vii)}$$

$p[\text{H}]$ of a solution of chromate-dichromate mixture may also be calculated using the equation (ia),

$$\frac{1}{[\text{H}^+]^2} = K \cdot \frac{[\text{CrO}_4^{2-}]^2}{[\text{Cr}_2\text{O}_7^{2-}]}$$

$$\therefore p[\text{H}] = \frac{1}{2} \log K + \frac{1}{2} \log \frac{[\text{CrO}_4^{2-}]^2}{[\text{Cr}_2\text{O}_7^{2-}]} \quad \text{..... (viii)}$$

Substituting the values of pK_1^H (6.53) and pK_2 (1.64) one may obtain, $\log K = 11.42$ (at 25°C). From equation (viii),

$$\therefore p[\text{H}] = 5.71 + \frac{1}{2} \log \frac{[\text{CrO}_4^{2-}]^2}{[\text{Cr}_2\text{O}_7^{2-}]}$$

If chromate ion is present in large excess and dichromate is less, say,

$$[\text{CrO}_4^{2-}] = 1M, [\text{Cr}_2\text{O}_7^{2-}] = 0.01 M$$

$$\therefore \frac{[\text{CrO}_4^{2-}]^2}{[\text{Cr}_2\text{O}_7^{2-}]} = \frac{(1)^2}{(0.01)} = 100$$

$$\therefore p[\text{H}] = 5.71 + \frac{1}{2} \log 100 = 6.71$$

If dichromate ion is present in large excess and chromate is less, say,

$$[\text{CrO}_4^{2-}] = 0.01M, [\text{Cr}_2\text{O}_7^{2-}] = 1M$$

$$\therefore \frac{[\text{CrO}_4^{2-}]^2}{[\text{Cr}_2\text{O}_7^{2-}]} = \frac{(0.01)^2}{1} = 10^{-4}$$

$$\therefore p[\text{H}] = 5.71 + \frac{1}{2} \log 10^{-4} = 3.71$$

Thus, if the pH of the aqueous extract of a sample is in the acidic region, dichromate will predominate and if the pH is in the neutral or alkaline region chromate will predominate.

Indication

(1) (i) Colour in the solid state and in solution

Orange colour — dichromate

Yellow colour — chromate

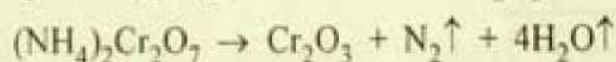
(ii) Acid-base nature of aqueous solution: (test with pH indicator paper)

Acidic ($pH < 4.5$) orange colour — dichromate

Neutral/alkaline ($pH > 6$), yellow colour — chromate.

(2) Action of heat

If heated in presence of a reducing agent, orange or yellow colour changes to green due to reduction to Cr_2O_3 . Ammonium dichromate on heating [CAUTION] decomposes with explosion and firing leaving a green residue of Cr_2O_3 .



Dichromate oxidizes NH_4^+ ion to set free N_2 gas and itself is reduced to Cr_2O_3 .

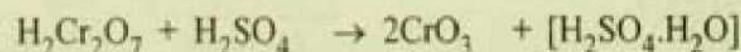
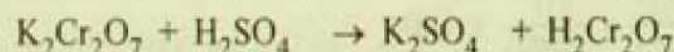
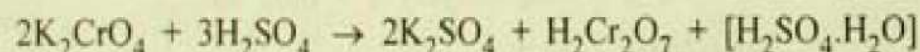
(3) Borax bead test

As borax ($Na_2B_4O_7 \cdot 10H_2O$) or its decomposition product, sodium metaborate ($NaBO_2$) form alkaline melt, chromate or dichromate imparts a dark yellow colour to the borax bead when heated on the oxidizing flame and a deep green colour due to reduction to $Cr(III)$ state when heated in the reducing flame.

(4) Concentrated sulfuric acid

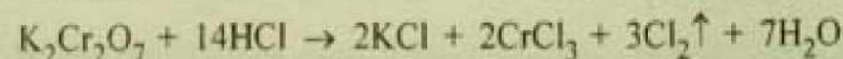
Dark brown colouration appears due to the formation of chromic acid (CrO_3).

CAUTION : Much heat is produced in this reaction.



(5) Concentrated hydrochloric acid

When heated with conc. HCl , the yellow or orange colour of chromate or dichromate changes, forming a green solution as $Cr(VI)$ is reduced to $Cr(III)$ salt by HCl , which is oxidized to chlorine gas.



(6) Hot concentrated sulfuric acid + chloride salt

Formation of brownish yellow chromyl chloride gas (*cf.* chromyl chloride test for chloride, p. 390).

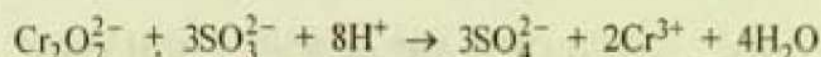
Reactions of Chromate/Dichromate ions in solution

(a) Reactions as Oxidizing agent/Reduction reactions

All reactions of chromate/dichromate as oxidizing agent take place in acid medium, in which orange coloured dichromate predominates and in all its reactions it is reduced to green coloured Cr(III) salts. All these tests are interfered by most other oxidizing agents.

(1) Reaction with SO₂-water/sulfite/bisulfite

In acid medium dichromate oxidizes sulfite to sulfate, which may be detected by barium chloride test.



Mix 1-2 drops of barium chloride and 1 ml of dil. (1:4) HCl and add a few drops of SO₂-water (or sodium sulfite or bisulfite solution) in a semi-micro test tube. No precipitate is formed. Now add a few drops of test solution (if orange or yellow coloured), and shake. A green coloured solution results and a heavy white precipitate (BaSO₄), appears.

(2) Potassium iodide-starch solution

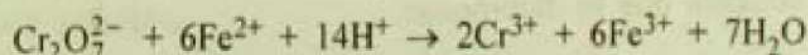
Dichromate in acid medium oxidizes iodide to set free iodine, which forms a deep blue coloured adsorption complex with starch (*cf.* test for iodide).



Place 1 drop of starch solution, 1 drop of (1:1) dil. HCl and a crystal of KI on a spot plate. No blue colouration will be observed. Now add a drop of the test solution. An intense blue colouration results. (*cf.* tests for iodide).

(3) Ferrous sulfate (or Mohr's salt) solution

In acid medium (~ 2N) dichromate oxidizes Fe(II) to Fe(III) and itself is reduced to green coloured Cr(III) salt.



Place 1 drop of Fe(II) salt solution and a crystal of NH₄SCN (or KSCN) on a cavity of a spot plate. No reaction/colouration occurs.

In another cavity of the spot plate, place 1 drop of the orange coloured acidic test solution, add drops of Fe(II) salt solution until the orange colour is discharged. Now add a crystal of NH₄SCN (or KSCN). An intense red colouration [due to Fe(SCN)²⁺] is produced.

(4) H₂S-water

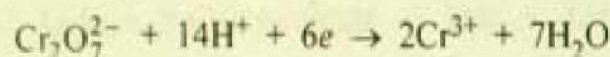
In acidic solution, dichromate is reduced to Cr(III) salt by H₂S, which is oxidized to elemental sulfur, that separates in milky colloidal form,



Take 1 ml of orange coloured acidic (dil.HCl) test solution in a semi-micro test tube and add drops of H₂S-water. The orange colour is discharged and a milky white turbidity appears. Add a few small pieces of filter paper strips or some asbestos pulp, boil for 2-3 minutes and then centrifuge. The green coloured Cr(III) salt solution now becomes clearly visible.

(5) Oxidation of alcohol

Dichromate in acid medium oxidizes ethanol to acetaldehyde, slowly in the cold, but rapidly on warming.



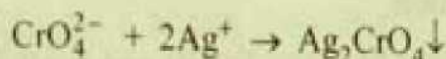
Take 1 ml of ethanol in a semi-micro test tube, add 1 ml of (1:4) dil. H₂SO₄ and a few drops of the yellow or orange coloured concentrated test solution. Plug the test tube with a piece of clean cotton wool (Fig. 3.27) and then place the test tube on hot water bath (Fig. 3.15) for a few minutes. Smell of acetaldehyde appears.

(b) Reactions involving precipitation

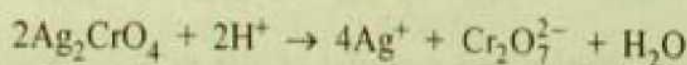
As most dichromates are soluble in water and only the chromates of certain metals are insoluble in neutral or weakly acidic (acetic acid) medium, most of the precipitation reactions with chromate/dichromate are carried out in neutral or weakly acidic (acetic acid) solution.

(1) Silver nitrate solution

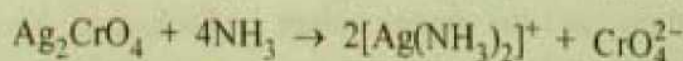
Place a drop of the neutral test solution in three semi-micro test tubes and add 1 drop of silver nitrate solution to each of the test tubes. Brownish red precipitate of silver chromate appears in all the three test tubes.



(i) Add a few drops of dil. HNO₃ in one of the test tubes. The precipitate dissolves, giving an orange coloured solution due to dichromate,

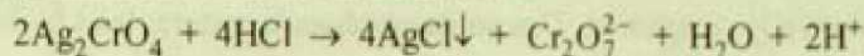


(ii) Add a few drops of dilute (1:1) aq-NH₃ to another test tube. The precipitate dissolves, due to the formation of [Ag(NH₃)₂]⁺ complex ion, producing a yellow solution of chromate,

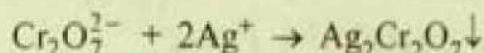


CAUTION : Discard the ammoniacal solution containing the complex $[\text{Ag}(\text{NH}_3)^+]$ ion immediately after test to avoid explosion.

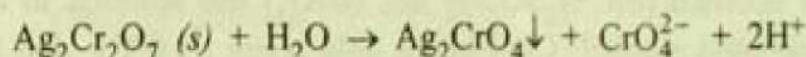
(iii) Add a few drops of dil. (1:1) HCl to the third test tube and digest the mixture for a few minutes on a hot water bath (Fig. 3.15). White precipitate of silver chloride appears, producing an orange coloured solution of dichromate.



In another test tube take a drop of concentrated, weakly acidic orange coloured (i.e. dichromate) test solution and add a drop of silver nitrate solution. A red brown precipitate of silver dichromate appears.

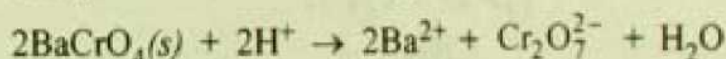
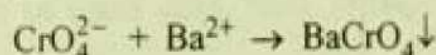


Centrifuge, and discard the centrifugate, wash the precipitate with cold water by centrifugation. Dilute the mixture with water and boil for a few minutes. The red-brown precipitate of silver dichromate is transformed to much less soluble silver chromate, and a yellow (CrO_4^{2-}) colour persists in the solution.

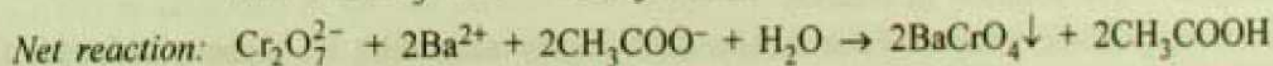
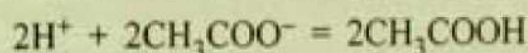
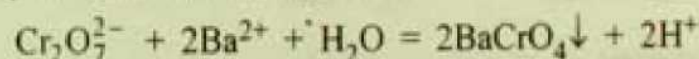


(2) Barium chloride (or nitrate) solution

To a drop of the yellow coloured neutral test solution (CrO_4^{2-}) add a drop of barium chloride (or nitrate) solution. Yellow precipitate of barium chromate appears. The precipitate is insoluble in water and acetic acid, but soluble in dilute mineral acids (HCl, HNO_3 etc.) producing orange coloured ($\text{Cr}_2\text{O}_7^{2-}$) solution :

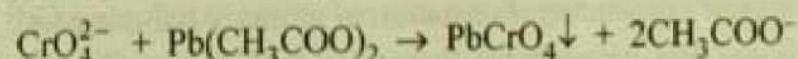


If the test solution itself is orange coloured ($\text{Cr}_2\text{O}_7^{2-}$), partial precipitation of yellow coloured barium chromate occurs. On addition of a few drops of dil. NaOH or sodium acetate solution, the precipitation becomes complete.



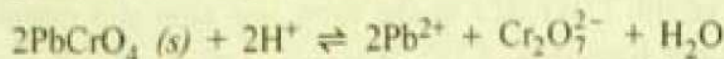
(3) Lead acetate solution

Take a drop of neutral or weakly acidic (acetic acid) test solution in three adjacent cavities of a spot plate and add 1 drop of lead acetate solution to each cavity. Yellow precipitate of lead chromate is formed in each cavity.

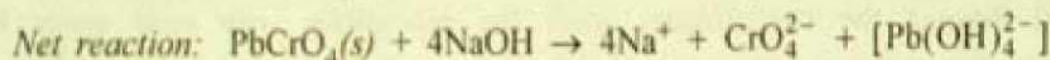
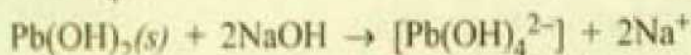
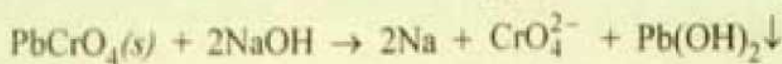


(i) To one of the cavities add a few drops of acetic acid, the precipitate does not dissolve.

(ii) To another cavity, add a few drops of dil. (1:1) HNO_3 . The yellow precipitate dissolves, producing an orange coloured ($\text{Cr}_2\text{O}_7^{2-}$) solution.



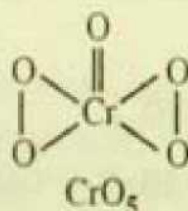
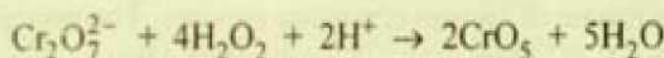
(iii) To the third cavity, add a few drops of dil. (2*N*) NaOH solution. The precipitate dissolves producing a yellow (CrO_4^{2-}) solution. Due to its amphoteric nature, lead hydroxide reacts with NaOH to form tetrahydroxoplumbate(II), $[\text{Pb}(\text{OH})_4]^{2-}$ ion. As a result, the equilibrium concentration of Pb^{2+} ion is lowered and solubility product of PbCrO_4 is not exceeded.



(c) Reactions involving colour formation: (Confirmation)

(1) Hydrogen peroxide (Perchromic acid test)

Take 1-2 drops of acidified (dil. H_2SO_4 or dil. HNO_3) test solution in a semi-micro test tube, add 1-2 *ml* of *iso*-amyl alcohol. Cool in ice cold water ($\sim 0^\circ\text{C}$) and then add 1 *ml* of 10-volume (3%) H_2O_2 solution. A deep blue colouration is produced due to the formation of peroxochromic acid (CrO_5) (1), which being more soluble in amyl alcohol, passes into the organic layer turning it blue coloured.



(1)

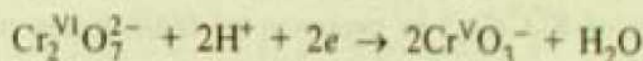
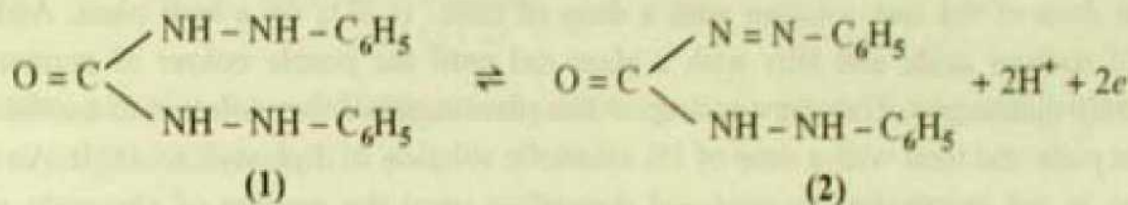


(2) 1,5-Diphenylcarbazide reagent

Reagent : 1% solution in ethanol.

In strongly acidic solution chromate (i.e. dichromate) reacts with 1,5-diphenylcarbazide (1) or with its oxidation product, 1,5-diphenylcarbazone (2) to produce an intense violet colouration. $\text{Cr}^{3+}(\text{aq})$ ion does not produce such violet colouration with either of the two forms (1) or (2) of the reagent. So the logic of oxidation of (1) to (2) by $\text{Cr}_2\text{O}_7^{2-}$ ion in acid medium with simultaneous reduction of $\text{Cr}(\text{VI})$ to $\text{Cr}(\text{III})$ and complex formation of $\text{Cr}(\text{III})$ with either (1) or (2) or both does not appear convincing. Formation of strongly reducing Cr^{II} under the aerobic condition of the experiment and its complex formation with (1) or (2) or both producing the

violet colouration also does not appear convincing, because of the very high intensity of the colouration that is normally not expected for d-d transition. However, a charge transfer transition of LMCT type involving Cr^{VI} or Cr^{V} as acceptor and the ligand (1) and or its oxidized form (2) as donor (s) appears to be more convincing in accounting for the high intensity of the violet colour of the resulting complex. Cr^{V} because of its coordinately unsaturated state, should act as a better acceptor.



$\text{L} = (1) \text{ and or } (2).$

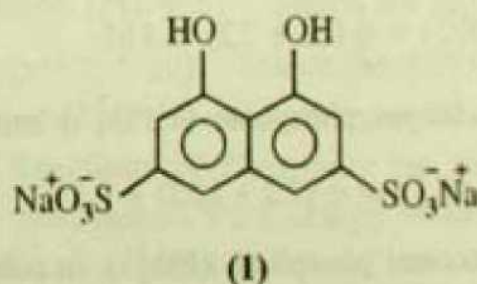
Limit of identification : 0.25 γ of Cr

Limit of dilution : 1 : 2×10^6 .

(3) Sodium salt of chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid)

Reagent : Dissolve 0.1g of the sodium (1,8-dihydroxy naphthalene-3,6-disulfonate) in 5 ml of water, mix thoroughly. Use the clear supernatant liquid with the help of a capillary tube and a piece of clean cotton wool (Fig. 3.19b). Use freshly prepared solution for the test.

Acid solution of chromate (i.e. dichromate) reacts with sodium salt of chromotropic acid (1) produces a red colouration if viewed through transmitted light. Fe, U and Ti interfere, but in the presence of nitric acid, their interfering actions are eliminated.



Possibly a charge transfer complex involving the phenolic (OH) groups of the reagent and $\text{Cr}(\text{VI})$ is responsible for the intense red colouration.

Place a drop of the yellow or orange coloured test solution in a semi-micro test tube, add 1 drop of dil. (8M) HNO_3 solution, dilute to $\sim 2 \text{ ml}$ and then add 1 drop of the reagent. A red colouration is produced which is best viewed with a white light source behind the test tube.

Limit of dilution : 1 : 5000.

(4) Test for Chromate/Dichromate in the presence of Permanganate

The intense purple colour of permanganate (MnO_4^-) ion, masks the yellow colour of

chromate (CrO_4^{2-}) and orange colour of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ions, as such even the sensitive diphenyl-carbazide test for chromate/dichromate can not be directly applied. Permanganate ion is readily reduced to almost colourless Mn^{II} salt by hydrazoic acid (or sodium azide), which has little effect on chromate/dichromate. Hydrazoic acid is oxidized by permanganate mainly to N_2 gas, small amounts of N_2O gas and nitrate are also possibly produced. Mn^{II} salt that is produced, does not interfere in the diphenylcarbazide test for chromate/dichromate.

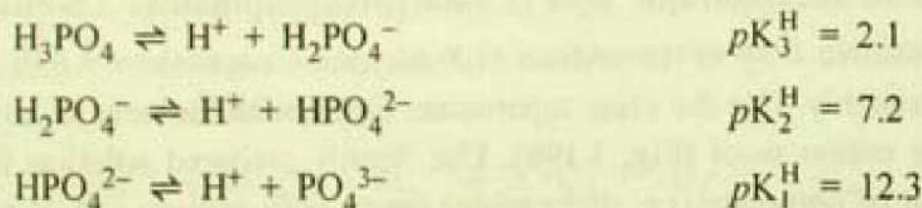
Mix a drop of the test solution with a drop of conc. H_2SO_4 on a spot plate. Add a few crystals of sodium azide and stir with a glass rod until the purple colour of permanganate is completely discharged. Transfer one drop of this permanganate free solution to another cavity of the spot plate and treat with a drop of 1% ethanolic solution of diphenylcarbazide. An intense blue-violet to red colouration is produced depending upon the amount of chromate present.

Limit of identification : 0.5% of K_2CrO_4 in presence of 6000 times of KMnO_4 .

Limit of dilution : 1 : 1×10^5 .

5.19 Reactions of Phosphate (PO_4^{3-} , HPO_4^{2-} , H_2PO_4^- , H_3PO_4)

Except sodium, potassium and ammonium salts, phosphates of most metals are sparingly soluble in water, but soluble in dilute mineral acids, as orthophosphoric acid (H_3PO_4) is a weak tri-protic acid (cf. Sect. 2.1) :



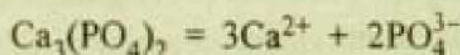
Consequently, aqueous solutions of dihydrogen phosphate (H_2PO_4^-) salts are very slightly acidic,

$$\text{pH} = \frac{1}{2}(pK_3^{\text{H}} + pK_2^{\text{H}}) = \frac{1}{2}(2.1 + 7.2) = 4.65$$

and aqueous solutions of monohydrogen phosphate (HPO_4^{2-}) salts react alkaline,

$$\text{pH} = \frac{1}{2}(pK_2^{\text{H}} + \frac{1}{2}pK_1^{\text{H}}) = \frac{1}{2}(7.2 + 12.3) = 9.75$$

Although it is difficult to obtain normal phosphate (PO_4^{3-}) in soluble form in water, but PO_4^{3-} ion may be present in saturated solution of sparingly soluble phosphates of certain metals:



Depending upon the solubility products, such solutions should be strongly alkaline,

$$\text{pH} = \frac{1}{2}pK_w + \frac{1}{2}pK_1^{\text{H}} + \frac{1}{2}\log[\text{PO}_4^{3-}]$$

For ionization of $\text{Ca}_3(\text{PO}_4)_2$,



$$\therefore [\text{Ca}^{2+}] = \frac{3}{2}[\text{PO}_4^{3-}]$$



Solubility product (K_{sp}) of $\text{Ca}_3(\text{PO}_4)_2$ may be defined as,

$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

$$\therefore K_{sp} = \left(\frac{3}{2}[\text{PO}_4^{3-}]\right)^3 \times [\text{PO}_4^{3-}]^2 = \left(\frac{3}{2}\right)^3 [\text{PO}_4^{3-}]^5$$

$$\text{Hence, } [\text{PO}_4^{3-}] = \left[\frac{K_{sp}}{(3/2)^3} \right]^{\frac{1}{5}}$$

Therefore, pH of a saturated solution of calcium phosphate will be [$\because \text{p}K_w = 14$, $\text{p}K_1^{\text{H}} = 12.3$ and $\text{p}K_{sp} = 32.67$ at 25°C]:

$$\begin{aligned} \text{pH} &= \frac{1}{2}(14) + \frac{1}{2}(12.3) + \frac{1}{2} \log \left[\frac{K_{sp}}{(3/2)^3} \right]^{\frac{1}{5}} \\ &= 13.15 + \left(\frac{1}{2} \times \frac{1}{5} \right) \log K_{sp} - \left(\frac{1}{2} \times \frac{1}{5} \times 3 \right) \log(3/2) \\ &= 13.15 - \frac{1}{10} \text{p}K_{sp} - \frac{3}{10} \log 1.5 \\ &= 13.15 - 0.1 \times 32.67 - 0.3 \times \log 1.5 = 9.83 \end{aligned}$$

Indication

There is no suitable indicative test for phosphate with solid samples.

(1) Acid-base nature of aqueous extract

Boil a small quantity ($\sim 0.1\text{g}$) of the solid sample with water in a semi-micro test tube, centrifuge and test the centrifugate with a pH indicator paper.

(i) Weakly acidic reaction (pH 4-5) : Search for H_2PO_4^-

(ii) Alkaline reaction (pH > 9-10) : Search for HPO_4^{2-} and PO_4^{3-}

Note : Carbonate, bicarbonate, fluoride also give alkaline reactions in aqueous solution.

Reactions of Phosphate ion in solution

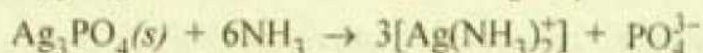
As the phosphates of most metals are sparingly soluble in water, it is convenient to test for phosphate with the sodium carbonate extract of the sample after neutralization with dilute nitric acid, or, with concentrated nitric acid extract of the sample as required.

A. Tests with Na_2CO_3 extract

Treat the Na_2CO_3 extract of the sample with dil. HNO_3 until, just acidic, boil to remove CO_2 . Add drops of dilute aq-NH_3 solution until just ammoniacal. Boil off excess ammonia and perform the following tests with this *prepared test solution* (or, neutralized Na_2CO_3 extract).

(1) Silver nitrate solution

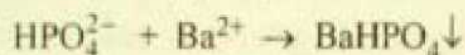
To 1-2 drops of the prepared test solution add 1 drop of AgNO_3 solution. Yellow precipitate of silver orthophosphate, (Ag_3PO_4) appears. The precipitate is soluble in dilute nitric acid and also in aq-NH_3 .



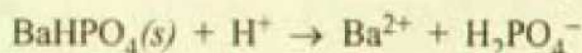
CAUTION : Discard the solution obtained after dissolving the precipitate of Ag_3PO_4 in ammonia quickly after test to avoid explosion (*cf.* tests for Ag^+ , and Cl^-).

(2) Barium chloride solution

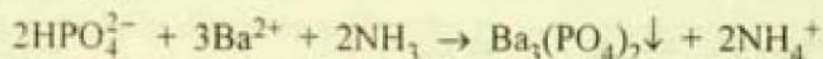
To 1 *ml* of the neutralized Na_2CO_3 extract of the sample add 1-2 drops of barium chloride solution. A white amorphous precipitate of barium hydrogenphosphate appears.



The precipitate is soluble in dilute mineral acids (HCl , HNO_3) and also in acetic acid.



If barium chloride solution is added to an ammoniacal test solution, tertiary barium phosphate is precipitated,

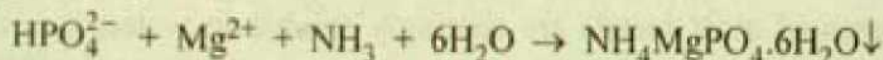


(3) Magnesia mixture (or Magnesium nitrate) reagent

Reagents : (i) Magnesia mixture ($\sim 0.5M$) : ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{Cl} + \text{NH}_3$). Dissolve $\sim 10\text{g}$ of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\sim 11\text{g}$ of NH_4Cl in water (50 *ml*) add 5 *ml* of conc. NH_3 and dilute to 100 *ml*.

(ii) Magnesium nitrate reagent ($0.5M$) : ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{NH}_4\text{NO}_3 + \text{NH}_3$). Dissolve $\sim 13\text{g}$ of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\sim 16\text{g}$ of NH_4NO_3 in water (50 *ml*) add 5 *ml* of conc. NH_3 and dilute to 100 *ml*.

To 1 *ml* of the neutralized Na_2CO_3 extract in a semi-micro test tube, add 1-2 drops of either of the above two reagents, add 1 drop of dilute ammonia if necessary, scratch the sides of the test tube with a glass rod. White crystalline precipitate of ammonium magnesium phosphate, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ appears,



The precipitate is insoluble in ammoniacal medium, but soluble in acetic acid and mineral acids (HCl , HNO_3).

Arsenate (AsO_4^{3-}) gives precipitate of ammonium magnesium arsenate $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$, under the same condition with both the reagents. However, phosphate and arsenate precipitates may be distinguished.

Distinction between Phosphate and Arsenate

Wash the white crystalline precipitate obtained on treatment of the neutralized Na_2CO_3 extract with magnesium nitrate reagent with water by repeated centrifugation. Treat the precipitate with silver nitrate solution containing a few drops of acetic acid.

The precipitate changes colour to :

- (i) yellow (due to Ag_3PO_4), if phosphate is present;
- (ii) brownish-red (due to Ag_3AsO_4), if arsenate is present.

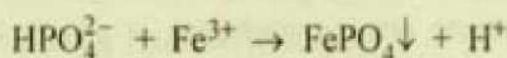
(4) Sodium acetate-Acetic acid-Ferrie chloride reagent

Reagents :

(i) Feric chloride (0.5M) : Dissolve ~ 13.5g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 30 ml of (1:1) HCl by warming, dilute to 100 ml. The solution is to be neutralized with (1:1) aq- NH_3 before use (cf. p-370, 491).

(ii) Sodium acetate-acetic acid buffer : Dissolve ~ 27g $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ in water, add 11.5 ml of glacial acetic acid, dilute to 100 ml (pH = 4-5).

Take 1 ml of the neutralized Na_2CO_3 extract in a semi-micro test tube, add 1 ml of sodium acetate-acetic acid buffer (pH ~ 4-5) solution, heat just to boiling and add 1 drop of neutral FeCl_3 solution. Yellowish white precipitate of FePO_4 appears :

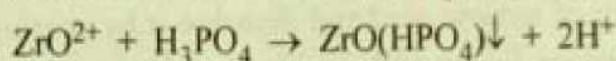


The precipitate is soluble in dilute mineral acids.

(5) Zirconyl nitrate reagent

Reagent : Boil ~ 10g of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ with 100 ml of 2M HNO_3 while stirring continuously. Allow to stand for 24 hours. Decant the clear supernatant liquid for use as the reagent.

If the acidity of the phosphate solution is not higher than 1M, zirconyl hydrogen phosphate is precipitated even from dil. HCl solution of phosphate.



Note : Depending upon the concentration of ZrO^{2+} ion and pH of the solution, the composition of the precipitate may be $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ or $\text{ZrO}(\text{HPO}_4)$ or $(\text{ZrO})_3(\text{PO}_4)_2$. (cf. p.-73)

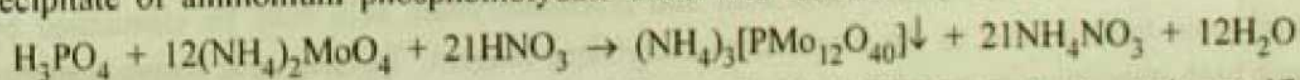
B. Tests with HNO_3 extract: (Confirmation)

(6) Ammonium molybdate reagent

Reagent : (cf. Sect. 4.8, arsenate).

Note : Commercial ammonium molybdate is the heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$. The formula $(\text{NH}_4)_2\text{MoO}_4$ is used in writing chemical equations for simplicity. The molybdate ion, MoO_4^{2-} , possibly exists under the experimental condition employed for testing phosphate.

In strong nitric acid medium and in presence of large excess of ammonium nitrate, phosphate (actually H_3PO_4) reacts with an excess of ammonium molybdate to produce a canary yellow precipitate of ammonium phosphomolybdate under hot condition (~40°C) :



The precipitate is soluble in ammonia and in caustic alkali. Reducing agents such as sulfide, sulfite, ferrocyanide etc. interfere, but if the test is carried out with the conc. HNO_3 extract of the sample, the reducing agents are oxidized to harmless products.

Arsenate gives similar yellow precipitate of ammonium arsenomolybdate $(\text{NH}_4)_3[\text{AsMo}_{12}\text{O}_{40}]$, with the ammonium molybdate reagent (*cf.* Sect. 4.8). But the yellow precipitate due to NH_4^+ -arsenomolybdate is formed on boiling the reaction mixture for a few minutes, whereas, the yellow precipitate due to NH_4^+ -phosphomolybdate is formed on just warming ($\sim 40^\circ\text{C}$) the reaction mixture.

To 1 drop of the HNO_3 extract of the sample in a semi-micro test tube, add 1 ml of the ammonium molybdate-ammonium nitrate-nitric acid reagent and place the test tube in a beaker of boiling water (Fig. 3.15). A beautiful canary yellow precipitate appears within a very short time if phosphate is present.

Wash the precipitate with water by repeated centrifugation, add a few crystals of tartaric acid and ~ 1 ml of water. Boil the mixture. Two cases may arise :

(i) If the yellow precipitate is due to ammonium phosphomolybdate, it remains unchanged, it does not dissolve.

(ii) If the precipitate is due to ammonium arsenomolybdate, it passes into solution.

Note : Tartaric acid forms such a stable complex with molybdic that only phosphoric acid can react with it to form a yellow precipitate, but arsenic acid, silicic acid can not.

(7) Molybdenum blue - Benzidine blue test

Reagents:

(i) Dissolve 0.5g of benzidine base or its chloride salt in 10 ml of glacial acetic acid and dilute to 100 ml with water.

(ii) Dissolve 5g of ammonium molybdate in 100 ml of cold water and add 35 ml of conc. HNO_3 slowly with stirring. Add 15g of tartaric acid and dissolve it by stirring. Allow to stand overnight. Decant the clear supernatant liquid and use it for the tests.

Molybdic acid or molybdate ion does not oxidize benzidine to benzidine blue (*cf.* Sect. 4.4). But heteropoly molybdic acids, viz. phosphomolybdic acid $[\text{H}_7\text{P}(\text{Mo}_2\text{O}_7)_6]$, arsenomolybdic acid $[\text{H}_7\text{As}(\text{Mo}_2\text{O}_7)_6]$ and silicomolybdic acid $[\text{H}_8\text{Si}(\text{Mo}_2\text{O}_7)_6]$ and their ammonium salts have such enhanced oxidizing power that they can oxidize benzidine to benzidine blue with concomitant reduction of molybdic acid to molybdenum blue. Even very dilute solution of phosphate, which does not form a visible precipitate with ammonium molybdate reagent, gives a distinct blue colouration with molybdic acid and benzidine.

Silicic acid reacts with molybdic acid under identical condition to produce soluble silicomolybdic acid, which also oxidizes benzidine to benzidine blue. Arsenic acid forms arsenomolybdic acid, of which the ammonium salt, ammonium arsenomolybdate forms a yellow precipitate like its phosphate analogue, also oxidizes benzidine to benzidine blue.

Interference due to silicomolybdic acid and arsenomolybdic acid may be eliminated by adding some tartaric acid to the ammonium molybdate reagent. Tartaric acid forms complex of such high stability with molybdic acid that neither silicic acid nor arsenic acid can decompose this complex, but it is decomposed by phosphoric acid to form phosphomolybdic acid.

Place a drop of the dilute HNO_3 extract of the sample on a drop reaction paper and add 1 drop of ammonium molybdate-tartaric acid reagent. Dry the spot by placing the filter paper

on a watch glass covering a beaker of boiling water. Add 1 drop of benzidine reagent and hold the paper over an open bottle of ammonia solution. A blue stain indicates phosphate. Run a blank test.

Limit of identification : 1.5γ of P_2O_5 .

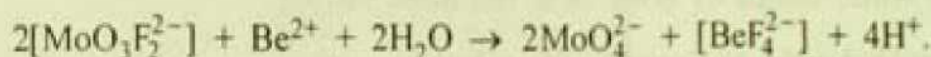
Limit of dilution : 1 : 3.3×10^4 ,

in presence of 500 times amount of $SiO_2 \cdot H_2O$.

Fluoride ion, if present, forms stable complex, $[MoO_3F_2]^{2-}$ ion with molybdate and interferes in the precipitation of phosphate as ammonium phosphomolybdate. Interference due to fluoride may be eliminated by either of the following procedures :

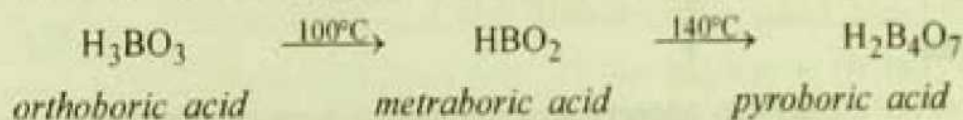
(i) Removing fluoride as volatile hydrogen fluoride (HF gas) by digesting the solid sample with conc. HCl and repeatedly evaporating to dryness in a **FUME CUPBOARD** (cf. fluoride removal Sect. 7.5), followed by taking up the residue with dil. HNO_3 . Silicic acid if present, is also removed as SiO_2 by this procedure.

(ii) On addition of beryllium nitrate (or chloride) solution, demasking of the $[MoO_3F_2]^{2-}$ complex ion takes place through the formation of $[BeF_4]^{2-}$ ion, based on the reaction :

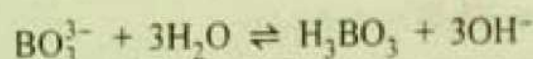
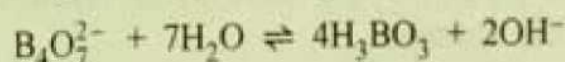


5.20. Reactions of Borates (BO_3^{3-} , BO_2^-), Boric Acid (H_3BO_3)

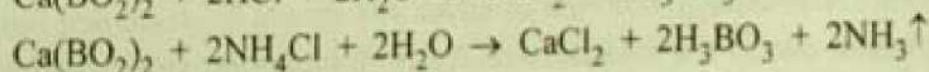
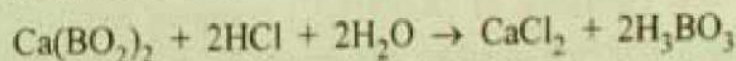
Three types of borate salts corresponding to three forms of boric acid may occur:



Salts of metaboric acid and pyroboric and are most common. Boric acids are all weak acids and borate ions are extensively hydrolysed giving alkaline solution (cf. p. 47).



Except alkali metal borates, all other borate salts are sparingly soluble in water, but they are fairly soluble in mineral acids and also in ammonium chloride solutions.

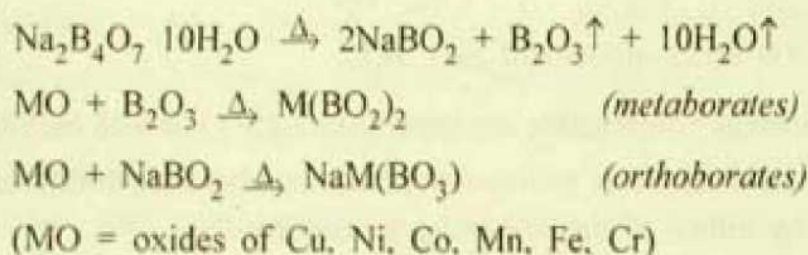


Indication

(1) Action of heat

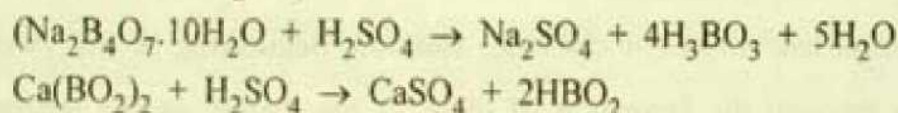
If free boric acid (H_3BO_3) is heated in a dry test tube, it volatilizes to form white fume. Borate salts on heating are transformed to metaborates, which often form molten transparent

mass. Transition metal borate salts form coloured melts. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) on heating in an ignition tube or on Pt-wire loop, first swells up, then subsides and finally transformed into a clear transparent bead of sodium metaborate (NaBO_2), which forms coloured mass with transition metals oxides (*cf.* Sect. 6.6 borax bead test).



(2) Concentrated sulfuric acid

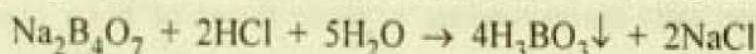
No visible reaction takes place in the cold, although boric acid is liberated from the reactions of borate salts with H_2SO_4



On heating, dense white fumes of boric acid becomes visible.

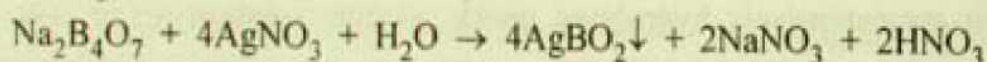
(3) Action of concentrated acid on borate salt solution

If a concentrated solution of borate salt (eg. borax) is treated with concentrated mineral acid (HCl , HNO_3 , H_2SO_4), boric acid is precipitated on cooling the solution.

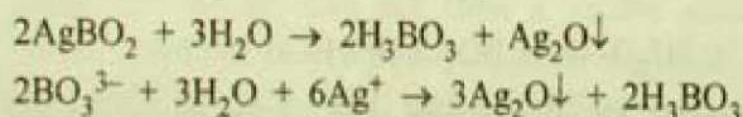


(4) Silver nitrate solution

White precipitate of silver metaborate appears on treatment of a concentrated solution of borax with AgNO_3 solution,



On boiling, the precipitate undergoes hydrolysis to form brown precipitate of silver oxide, which is directly formed in very dilute solutions,

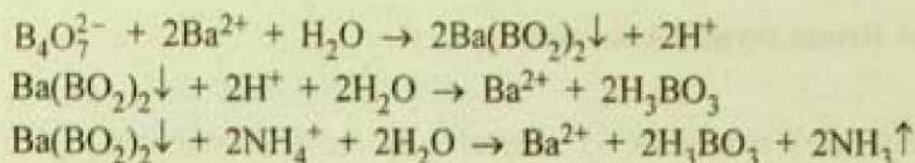


Precipitated silver metaborate (AgBO_2) is soluble in acetic acid. It is also soluble in ammonia solution due to the formation of $[\text{Ag}(\text{NH}_3)_2]^+$ complex ion.

CAUTION : Ammoniacal solution of silver salt should be discarded immediately after test to avoid explosion due to the formation of Ag_3N (*fulminating silver*) which is formed slowly.

(5) Barium chloride solution

White precipitate of barium metaborate $\text{Ba}(\text{BO}_2)_2$ appears on addition of BaCl_2 solution to a solution of borate. The precipitate is soluble in dilute mineral acids and also in solution of ammonium salts :



Calcium and strontium chloride solutions react similarly.

Confirmation

(1) Concentrated H_2SO_4 and alcohol (flame colouration)

(a) Mix a small amount ($\sim 0.2\text{g}$) of the dry sample with $\sim 2\text{ ml}$ of alcohol (methanol or ethanol, the former is preferred due to its greater volatility) and a few drops of conc. H_2SO_4 in a semi-micro test tube. Fix a bent glass tube with a cork at the mouth of the test tube (Fig. 3.30a). Warm the test tube gently by placing in a hot water bath (Fig. 3.15) and ignite the issuing gas in a non-luminous flame of a Bunsen burner. The gas burns with a green edged flame if borate or boric acid is present.

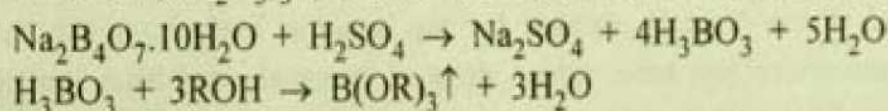
(b) Perform the above test (a) without adding conc. H_2SO_4 . If a green edged flame is produced, free boric acid is present, not borate.

The above observations are summarised below :

Sample + alcohol + conc. $\text{H}_2\text{SO}_4 \xrightarrow{\Delta}$ issuing gas burns with green edged flame
 $\rightarrow$ borate, boric acid.

Sample + alcohol $\xrightarrow{\Delta}$ issuing gas burns with green edged flame
 $\rightarrow$ boric acid only.

Boric acid is set free when conc. H_2SO_4 reacts with borate salts. Free boric acid reacts with alcohols in presence of conc. H_2SO_4 to produce volatile borate esters, e.g. methylborate, $\text{B}(\text{OCH}_3)_3$ or ethylborate, $\text{B}(\text{OC}_2\text{H}_5)_3$ (**POISONOUS**), which burns with green edged flame:

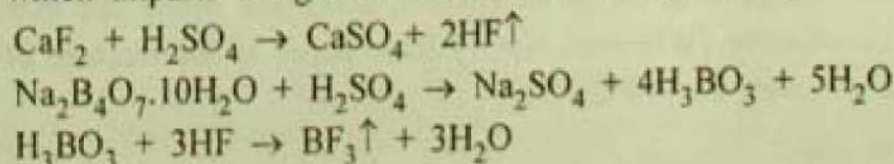


Cu and Ba salts produce similar green colouration of the Bunsen flame.

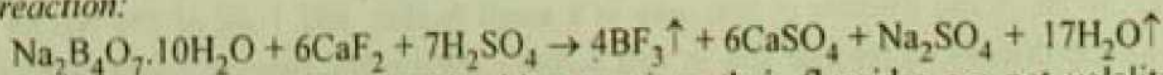
(2) Concentrated H_2SO_4 + CaF_2 (or NaF) test

Mix a small quantity ($\sim 0.2\text{g}$) of the dry sample with one third of its weight of CaF_2 (or NaF) on a watch glass and add a few drops of concentrated H_2SO_4 . Mix with a glass rod to make a thick paste. Hold the glass rod with the paste at its end close to the base of the non-luminous flame of a Bunsen burner avoiding physical contact with the flame. The colour of the flame turns green if borate or boric is present.

Boric acid and hydrogen fluoride produced *in situ* by the reactions of conc. H_2SO_4 with borate and fluoride salts respectively, react among themselves to produce volatile boron trifluoride (BF_3), which imparts the green colour to the Bunsen flame.



Net reaction:



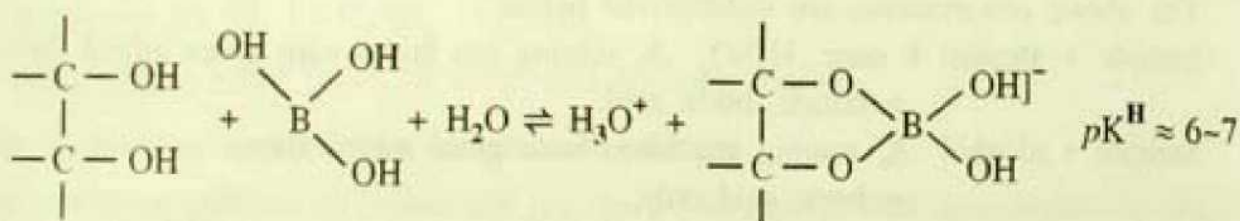
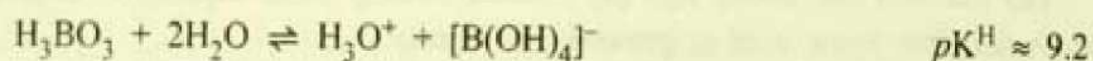
Cu and Ba salts do not interfere in this test, since their fluorides are not volatile.

(3) Mannitol-Bromothymol blue test

Reagents :

- (i) Bromothymol blue (0.04%) : Dissolve 40 mg of bromothymol blue in 100 ml of 95% ethanol.
- (ii) Mannitol (10%) : Dissolve 10g of mannitol ($C_6H_{14}O_6$) in water, add 1-2 drops of bromothymol blue indicator and neutralize the solution with dilute NaOH ($\sim 0.01M$) solution until the yellow colour of the solution just turns blueish green. Dilute the solution to 100 ml.

Boric acid (H_3BO_3) is a weak monoprotic acid ($pK^H \approx 9.2$) in aqueous solution. In presence of polyhydroxy organic compounds having two hydroxyl groups on adjacent C-atoms in *cis*-positions (ie. 1,2 *cis*-diols such as, mannitol, glycerol, dextrose or invert sugar etc.), acidity of aqueous solution of boric acid is increased due to chelate formation with boron (3+), arising out of its tendency to achieve tetracoordination (*cf. p-47*).



Enhancement of acidity (i.e. lowering of pH of the solution) is indicated by the change of colour (blueish green to yellow) of bromothymol blue indicator (pH range 6-7.6).

Take 1-2 ml of the Na_2CO_3 extract (or the aqueous extract, as the case may be) of the sample in a semi-micro test tube, add 1 drop of bromothymol blue indicator and neutralize with dil. HCl or dil. NaOH solution as required to adjust at a just blueish green colour. The solution is now neutral with respect to bromothymol blue indicator. Place 1-2 drops of this neutralized solution on a spot plate and add a few drops of the mannitol reagent solution. The blueish green colour of the solution changes to yellow if borate or boric acid is present.

Run a black test using distilled water in place of the sample solution.

Limit of identification : 0.001γ of B

Limit of dilution : 1 : 3×10^7 .

(4) Test with Turmeric (Curcuma)

Reagents : (i) Tincture of curcuma (or turmeric) paper :

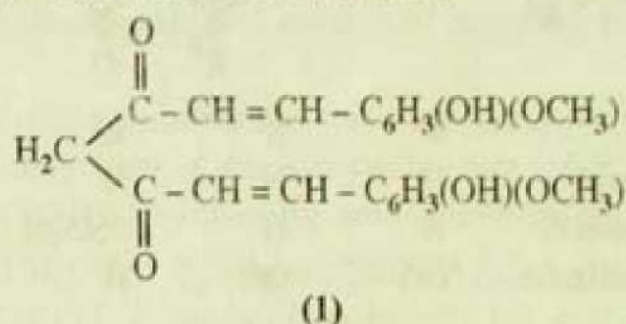
Boil 20g of curcuma with 50 ml of ethanol, filter and dilute the extract with 50 ml of water. Soak a quantitative (Whatman No. 1) filter paper in the tincture of curcuma and dry the paper in an air oven ($< 100^\circ C$).

(ii) Curcuma silk :

Take 50 ml of the tincture of curcuma in a small beaker, add 1 ml of 5% NaOH solution and soak the threads of viscose silk in this solution. Warm the threads gently until the mass

becomes syrupy. Immerse the threads into 100 ml water containing 1 ml of ethanol. Press the threads between filter papers. Bath the threads in dilute H_2SO_4 for some time, wash with water and dry in air.

Boric acid reacts with yellow coloured curcumin (diferuloylmethane) (1) and transforms it into the isomeric red brown coloured rosocyanine. A loose adsorption product between curcumin and boric acid is formed as an intermediate.



On treatment with alkali, the red-brown rosocyanine turns blueish black or greenish black. The original red-brown colour is restored on acidification.

Although Fe(III) , [molybdate, Ti(IV) , ZrO^{2+}]* compounds also react with curcuma giving red-brown products, but unlike that derived from boric acid, these coloured products do not change colour on treatment with alkali. Oxidizing agents (eg. chromate, nitrite, H_2O_2 etc.) and also iodide interfere. These must be removed or decomposed before performing this test.

(i) Place 1 drop of the test solution acidified with HCl on a curcuma paper and dry at $\sim 100^\circ\text{C}$ in an air oven. A red-brown spot results. Add 1 drop of 1% NaOH solution to the spot. The colour of the spot changes from red-brown to blue or greenish black. Add 1-2 drops of dilute (1:1) HCl . The red-brown spot reappears.

Limit of identification : 0.02γ of B

Limit of dilution : 1 : 2.5×10^6 .

(ii) Alternatively, place a drop of the test solution (or Na_2CO_3 extract) in a clean porcelain crucible add drops of dilute (1:1) HCl to acidify the solution. Place a silk thread impregnated with the curcuma reagent into this acidified solution and evaporate gently on a hot water bath. The thread is coloured pink-violet if borate is present. Bring the thread in contact with a dilute NaOH solution (1%). The colour changes to intense blue.

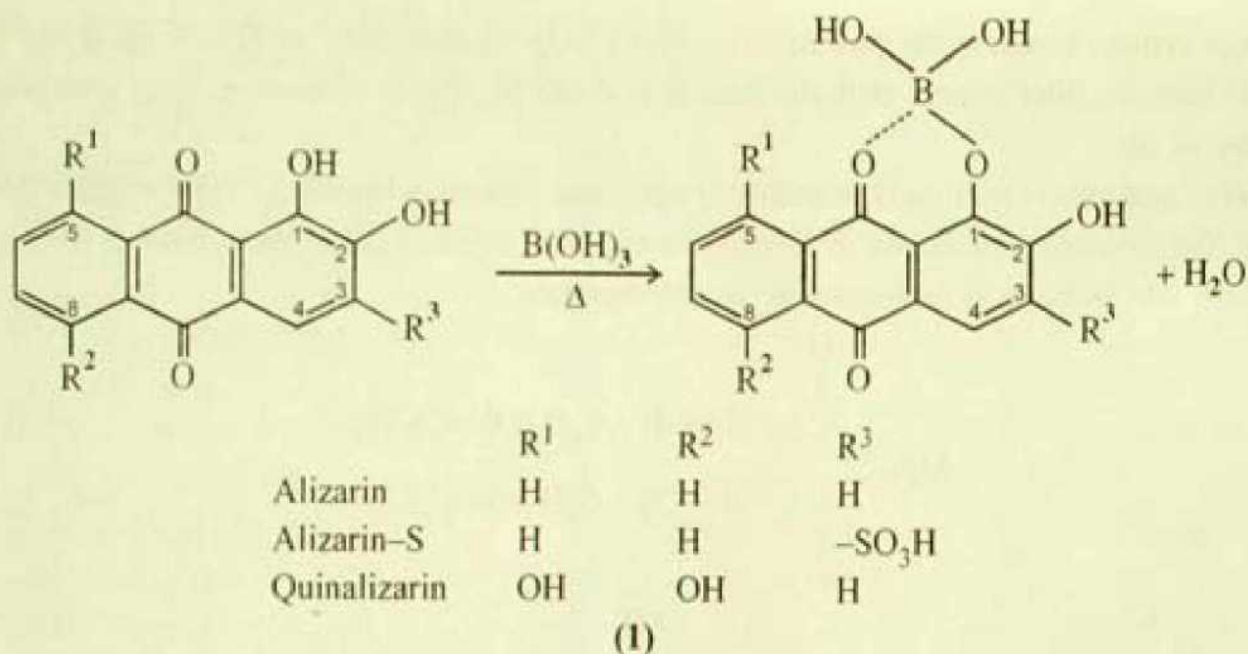
$[\text{Ti}, \text{Zr}, \text{Mo}, \text{W}, \text{and Ta}]^*$ salts do not interfere with this test if it is carried out in this manner.

(5) Test with hydroxyanthraquinones (Quinalizarin, Alizarin, Alizarin-S)

Reagents : (already described, cf. Mg^{2+} , Al^{3+} tests, cf. Ch-4).

Water insoluble hydroxyanthraquinones (1) dissolve in conc. H_2SO_4 producing deep coloured solutions, which give characteristic colour changes with boric acid, due to the formation of inner complex boric acid esters involving the OH^- groups in the peri-positions (2). Conc. H_2SO_4 in these reactions acts as a dehydrating agent.

*Rare elements



Take a drop of the slightly alkaline test solution (Na₂CO₃ extract) on a porcelain basin, evaporate to dryness. Treat the residue with 2-3 drops of the reagent solution and warm gently on a hot water bath. [Evaporation has to be done in alkaline condition to avoid loss of boric acid with steam]. Depending upon the reagent used, the following colour change takes place if boric acid or borate is present :

Alizarin :	yellow to red
Alizarin-S :	yellowish red to red
Quinalizarin :	violet to blue

Sensitivity of the test is lowered by Be²⁺.

Sb(III) gives similar colouration as boric acid. Sb (III), if present, should be oxidized to Sb (V) by Cl₂-water. Large quantities of coloured ions, eg. Cr³⁺, Fe³⁺, Co²⁺, Ni²⁺, Cu²⁺ interfere with the test. Oxidizing acids (HNO₃, HNO₂ etc.) impair the test. These may be eliminated by adding a crystal hydrazine sulfate before adding the reagent. Iodide interferes by liberating iodine. Iodide may be precipitated as harmless AgI by adding Ag₂SO₄ solution.

Limit of identification : 1.0, 1.0 and 0.6γ of B with alizarin, alizarin-S and quinalizarin respectively.

(6) Test by saponification of methylborate with alkali fluoride solution

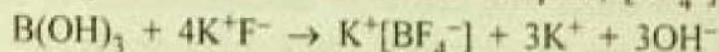
Reagents:

(i) Manganous nitrate-silver nitrate-alkali fluoride solution :

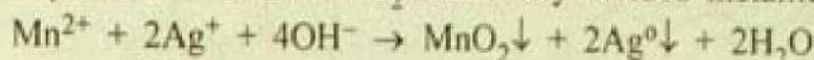
Dissolve ~ 2.9g of Mn(NO₃)₂ and ~ 1.7g of AgNO₃ in 100 ml of water, add one drop of dilute (~ 1M) NaOH solution, stir to mix uniformly. Filter any black precipitate formed at this stage. Add a solution of 3.5g of KF in 50 ml of water to the clear filtrate and warm gently for a few minutes. A white precipitate, that is initially formed, turns gray. Cool to room temperature and filter again. Use the clear filtrate for the tests.

(ii) Benzidine solution : Dissolve 0.05g of benzidine base or its hydrochloride in 10 ml of acetic acid and dilute to 100 ml with water and then filter. Use the clear filtrate as the reagent.

Boric acid reacts with aqueous solution of alkali fluoride giving an alkaline reaction due to the formation of very stable tetrafluoroborate complex, $[\text{BF}_4^-]$ ion :

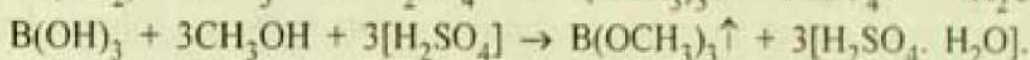
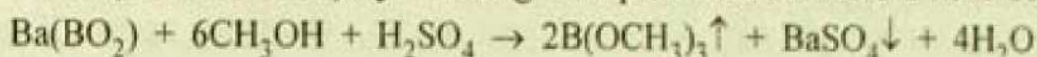


The free alkali (OH^- ions) forms a black precipitate with manganese nitrate-silver nitrate reagent, due to precipitation of black MnO_2 and finely divided metallic silver.



MnO_2 subsequently oxidizes acetic acid solution of benzidine to benzidine blue (cf. Sect. 4.4 and 4.16).

Both boric acid and borates respond to this test. The acid or the borate salt should be first separated from the remaining part of the sample by converting beforehand into volatile methylborate ester (**POISONOUS**) by warming with pure methanol and a little conc. H_2SO_4 .



The methylborate ester (b.p. 65°C) is distilled into an absorbing liquid consisting of the reagent solution and alkali fluoride. The ester is saponified to set free boric acid,



which reacts with alkali fluoride to form the $[\text{BF}_4^-]$ complex, liberating alkali (OH^- ion) due to profound tendency of B(3+) to achieve 4-coordination and very strong affinity of hard B(3+) cation for hard base F^- ion.

Take a small quantity ($<0.1\text{g}$) of the test sample or 1-2 drops of the test solution (plus 1 drop of $\sim 1\text{M}$ NaOH if the test solution is acidic), or 1-2 drops of the Na_2CO_3 extract in a semi-micro distillation apparatus (Fig. 3.31). Evaporate to dryness if the test sample is a solution. Add 5 drops of pure methanol and 5 drops of conc. H_2SO_4 . Stopper the apparatus with the distillation tube and attach a receiver containing the manganous nitrate-silver nitrate-potassium fluoride reagent solution. Adjust the height of the absorbing solution so that the end of the distillation tube just dips into it as in Fig. 3.31. Now heat the contents of the distillation tube to $\sim 80^\circ\text{C}$ by placing it on a hot water bath (Fig. 3.15). Methylborate distills into the receiver and is saponified, setting free alkali, which reacts with Mn^{2+} and Ag^+ to form the black precipitate of MnO_2 and Ag^0 if borate or boric acid is present.

Now dismantle the apparatus. Centrifuge the contents of the receiver and wash with water. Transfer a drop of the black slurry on a spot plate with the acid of a dropper pipette. Add a few drops of acetic acid solution of benzidine reagent. Traces of MnO_2 in the slurry is revealed by the appearance of blue colour. This method is recommended for detecting very small quantity of borate/boric acid.

Limit of identification : 0.01γ of B

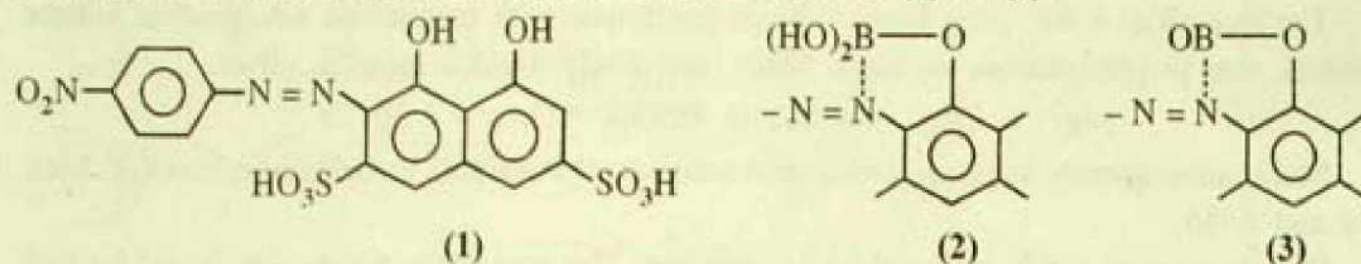
Limit of dilution : $1 : 5 \times 10^6$.

(7) 4-Nitrobenzene-azo-chromotropic acid (i.e. Chromotrope 2B) reagent

Reagent : 0.005% of chromotrope 2B in concentrated H_2SO_4 .

Chromotrope 2B (**I**) has an esterifiable phenolic OH -group in a chelating position with a

N-atom of the azo group. In presence of conc. H_2SO_4 , which functions as a dehydrating agent, the blue-violet coloured reagent reacts with ortho- or meta-boric acid to form greenish blue coloured inner chelate esters having the structural features (2) or (3).



Fluorides interfere by forming volatile BF_3 or fluoroboric acid (HBF_4), as a result, the borate esters can not be formed. Fluorides, if present, should be removed by volatilization as SiF_4 by digesting the sample with silica and conc. H_2SO_4 . Oxidising agents, if present, may be rendered harmless by adding a crystal of hydrazine sulfate to the test solution before adding the reagent.

Limit of identification : 0.08γ of B (in 0.04 ml)

Limit of dilution : 1 : 5×10^5 .

(i) Place a drop of the slightly alkaline test solution (Na_2CO_3 extract) on a porcelain dish, evaporate the solution to dryness on a hot water bath and while still hot, add 2-3 drops of the reagent solution and stir with a glass rod. Cool to room temperature. If boric acid (or, borate) is present, the colour changes from blue-violet to greenish blue. Run a blank test using a drop of distilled water in place of the test solution.

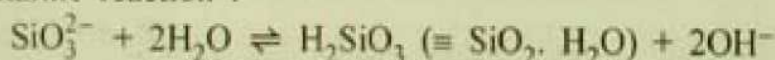
(ii) If any oxidising agent and fluoride ion are present :

To 1-2 drops of the test solution on a porcelain basin, add 1 or 2 crystals of hydrazine sulfate, very small quantity of silica and 1-2 drops of conc. H_2SO_4 . Heat the mixture gently in a **FUME CUPBOARD** until the dense white fumes of sulfur trioxide appear. Cool somewhat and while still hot, add 3-4 drop of the reagent solution to the residue. Note the colour change after cooling. If boric acid or borate is present, the colour changes from blue-violet to greenish blue.

Limit of identification : 0.25γ of B in presence of 11600 times of KClO_3 , 13,000 times of KNO_3 and 0.5γ of B in presence of 2700 times of NaF.

5.21. Reactions of Silicate (SiO_3^{2-}), Silica (SiO_2), Silicic Acid ($x\text{SiO}_2 \cdot y\text{H}_2\text{O}$)

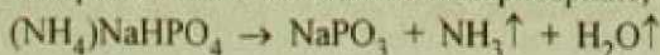
Except the silicates of the alkali metals, all other silicates, silica and silicic acid are insoluble in water. Silicic acid being a weak acid, soluble silicates are extensively hydrolyzed in aqueous solution giving alkaline reaction :



Indication

(1) Microcosmic salt bead test

When microcosmic salt, $(\text{NH}_4)\text{NaHPO}_4 \cdot 4\text{H}_2\text{O}$ is strongly heated, it first melts and then transforms into a transparent mass of sodium metaphosphate, NaPO_3 .



If a red hot platinum wire loop is touched with microcosmic salt, small amount of the salt adheres to the platinum loop, and on heating on a Bunsen flame, a transparent bead of sodium metaphosphate is produced on the platinum loop. If the red hot NaPO_3 bead is brought into contact with a silicate material, (eg. CaSiO_3) the latter adheres to the bead. When this mixture is strongly heated, silica (SiO_2) is set free due to the reaction :

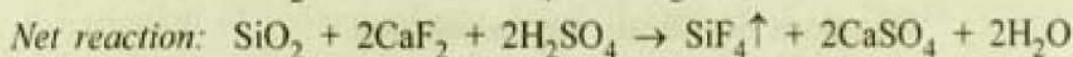
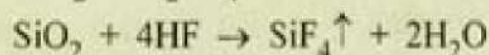


SiO_2 does not dissolve in the fused mass, but floats on the molten bead and its movement on the fused mass is clearly visible.

Form a loop at the head of a clean platinum wire. Heat on a Bunsen flame to dull redness and introduce the red hot loop into microcosmic salt powder. Heat the wire with the adhering salt strongly. Repeat these operations 2-3 times until a clear transparent bead is produced. Now touch the red hot bead with the powdered sample, so that a small amount of the sample adheres to the bead. Heat strongly until the mass is fused again. Movement of a opaque mass (SiO_2) on the transparent bead indicates SiO_2 .

(2) Silicon tetrafluoride test

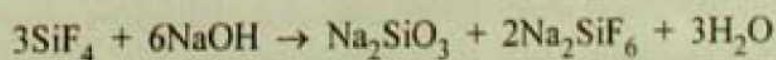
Silica and silicic acid react with hydrogen fluoride (HF) to produce volatile silicon tetrafluoride (SiF_4). If SiF_4 vapour is brought into contact with a drop of water, it dissolves in water precipitating hexafluorosilicic acid (H_2SiF_6) and silicic acid, which render the water drop opaque. Hydrogen fluoride may be generated *in situ* by the reaction of a fluoride salt (CaF_2 or NaF) with conc. H_2SO_4 .



Since glass is made of silicates, this test can not be conducted in a glass test tube. This test has to be carried out in a small lead or in a platinum capsule. Large excess of CaF_2 or NaF should be avoided, as large quantity of HF (or H_2F_2 etc.) interfere in the test. Borate and boric acid, if present, should be removed by warming the sample with methyl alcohol and a little conc. H_2SO_4 before applying the silicon tetrafluoride test for silicate.

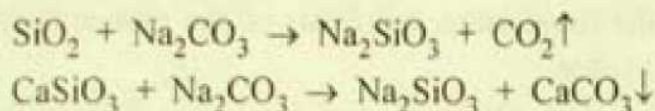
Mix small amount of the powdered sample (~ 0.2-0.4g) with one third of its weight of CaF_2 (or NaF) in a platinum or a lead capsule (or crucible), add drops of conc. H_2SO_4 to form a thin paste. Mix the contents with a stout Pt-wire. Cover the crucible with its lid having a small hole. Place the crucible on an asbestos board and heat gently in a **FUME CUPBOARD**. Hold a drop of water supported on a Pt-wire loop close to the hole of the crucible lid. The drop of water turns opaque.

If instead of a drop of water, a drop of NaOH solution is held to the issuing SiF_4 gas, soluble sodium silicate and hexafluorosilicate are formed :

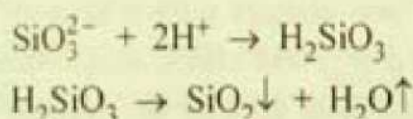


Treatment of insoluble silicate materials

Insoluble silicate materials and silica may be brought into solution by fusing with anhydrous sodium carbonate in a platinum foil or in a platinum crucible. In semi-micro scale, this can also be done with a platinum wire loop, by forming a molten bead of anhydrous sodium carbonate it on. Molten sodium carbonate reacts with insoluble silica and silicates to form soluble sodium silicate:



After cooling the melt, the resulting sodium silicate may be extracted with water, producing sodium silicate solution. Otherwise the cold mass may be treated with (1:1) HCl, when silicate is precipitated as hydrated silica or silicic acid and the metallic oxides and carbonates dissolve in HCl to produce the chloride salts. The precipitated hydrated silicic acid, because of its colloidal nature, is difficult to separate by filtration or centrifugation. On repeated digestion with conc. HCl followed by backing, it is transformed into granular silica (SiO_2), which can be obtained free from adhering soluble materials (chloride salts of metals) by washing with water by centrifugation.

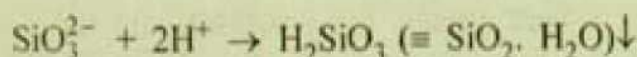


Both the solution of sodium silicate and silica obtained in this way may be subjected to confirmatory tests. Tests of silicate ion in solution may be carried out with the water extract of the Na_2CO_3 fusion melt (i.e. sodium silicate).

Reactions of Silicate ion in solution

(1) Dilute hydrochloric acid

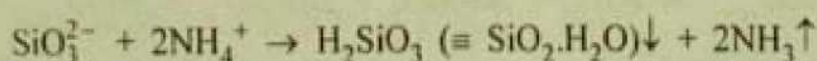
When a soluble silicate solution is acidified with dil. HCl, gelatinous precipitate of meta silicic acid (H_2SiO_3 , commonly known as silicic acid) is formed. Because of its colloidal nature, the precipitate of silicic acid takes long time to settle. In fact, if a dilute solution of sodium silicate (<10%) is added to a moderately concentrated solution of HCl, the resulting silicic acid is not precipitated, it remains in colloidal form. The colloidal silicic acid coagulates and settles quickly on boiling the acidified solution of silicate.



Note : Silicate interferes with the tests of Ag^+ , Pb^{2+} , Hg_2^{2+} with dil. HCl in Group-I.

2. Ammonium chloride or Ammonium carbonate solution

Silicate solution is alkaline due to hydrolysis of silicate ion. In presence of ammonium salts, alkalinity of silicate solution is neutralized due to acidic nature of NH_4^+ ion, and silicic acid is precipitated with evolution of ammonia gas.



Note : Silicate interferes with the tests of metal ions of which the hydroxides are precipitated on treatment with NH_4Cl and NH_3 solution, eg, Fe^{3+} , Al^{3+} , Cr^{3+} and with those precipitating as carbonates on treatment with ammonium carbonate eg. Ca^{2+} , Sr^{2+} , Ba^{2+} .

(3) Silver nitrate solution

Soluble silicates react with silver nitrate solution producing yellow precipitate of silver silicate,



The precipitate of silver silicate is soluble in ammonia solution due to the formation of $[\text{Ag}(\text{NH}_3)_2]^+$ complex ion. Precipitated silver silicate also dissolves in dil. HNO_3 , but silicic acid that is formed in the solution is precipitated [cf. reaction (1)].

CAUTION : Discard immediately the solution obtained by dissolving the precipitate of silver silicate in ammonia to avoid explosion.

(4) Barium chloride or Calcium chloride solution

White precipitate of barium (or calcium) silicate is formed when a silicate solution is treated with BaCl_2 (or CaCl_2) solution.



Precipitated BaSiO_3 (or CaSiO_3) is soluble in dilute HNO_3 .

Confirmation

The confirmatory tests of silicate should be performed with the insoluble silica residue or the solution of sodium silicate obtained from Na_2CO_3 fusion extract of the sample.

(1) Microcosmic salt bead test

Perform the test with the silica residue following the procedure as described before.

(2) Silicon tetrafluoride test

Perform the test with the silica residue following procedure described before.

(3) Benzidine blue-Molybdenum blue test

Silicomolybdic acid, $\text{H}_4[\text{SiMo}_{12}\text{O}_{40}]$ or $\text{H}_8[\text{Si}(\text{Mo}_2\text{O}_7)_6]$, like phosphomolybdic acid and arsenomolybdic acid, oxidizes benzidine to benzidine blue and itself is reduced to molybdenum blue (cf. Sect. 5.19 tests for phosphate), although molybdic acid itself does not oxidize benzidine. But unlike the ammonium salts of phosphomolybdic and arsenomolybdic acids, ammonium salt of silicomolybdic acid is soluble in water. Therefore, if ammonium molybdate is added to a solution of silicate, the resulting ammonium silicomolybdate remains in solution forming a yellow colouration, whereas, if phosphate or arsenate is present, yellow precipitate of ammonium phosphomolybdate or ammonium arsenomolybdate is formed, which may be separated from silico molybdate solution by centrifugation or by capillary separation using as capillary tube and a piece of pure cotton wool. The centrifugate may be tested for silicate.

(i) Place a drop of the clear liquid obtained after separation of any yellow precipitate resulting from the reaction of ammonium molybdate and the nitric acid test solution on a spot plate, add 2 drop of 1% oxalic acid solution to decompose residual phosphomolybdate if any (or a crystal of tartaric acid to decompose residual arsenomolybdate if any) which has but little action on silicomolybdate complex. Add 1 drop of 0.05% benzidine reagent in dil. (1:10) acetic acid and a few crystals of sodium (or ammonium) acetate. A blue colouration is formed if silicate is present. Compare with a blank, adding all the reagents except the test solution.

Limit of identification : 6γ of SiO_2

Limit of dilution : 1 : 8300.

(ii) Alternatively, place 1-2 drops of the aqueous extract of the Na_2CO_3 fusion melt (i.e., the solution containing sodium silicate) on a good quality porcelain crucible, acidify with nitric acid (final acidity $<0.5\text{ N}$), add a crystal of tartaric acid and 2 drops of 1% oxalic acid and 2-3 drops of the ammonium molybdate reagent, warm gently to remove effervescence if any. Cool to room temperature and add 1 drop of the benzidine reagent and a few crystals of sodium (or ammonium) acetate. A blue colouration appears if silicate is present. Compare with a blank.

Limit of identification : 0.1γ of SiO_2

Limit of dilution : 1 : 5×10^6 .

(iii) Alternatively, take the opaque residue formed in the water drop supported on a platinum wire loop, held in the issuing gas in the silicon tetrafluoride test, and place the same on a spot plate, add 1 drop of dil. HNO_3 , 2-3 drops of ammonium molybdate reagent, 1 drop of benzidine reagent and a few crystals of sodium (or ammonium) acetate. A blue colouration appears if silicate is present. Compare with a blank.

This test is most confirmative, since phosphate, arsenate which also respond to benzidine blue test can not interfere, as the test is conducted with volatilized silicon tetrafluoride, which is free from phosphate and arsenate. Borate interferes by forming volatile BF_3 . If borate or boric acid is present, remove them from the sample by warming with methanol and conc. H_2SO_4 before performing the silicon tetrafluoride test.

Limit of identification : 1γ of SiO_2 .

Limit of dilution : 1 : 5×10^4 .

(4) Ammonium molybdate-Stannous chloride test

When silicate is separated from the sample by volatilization as silicon tetrafluoride, by heating the sample with CaF_2 (or NaF) and conc. H_2SO_4 in a Pt or a Pb-capsule (crucible) and the resulting SiF_4 gas is absorbed in a drop of sodium hydroxide solution supported on a platinum wire loop, soluble sodium silicate and sodium hexafluorosilicate (cf. silicon tetrafluoride test, described before) are formed. If the sodium silicate and sodium hexafluorosilicate mixture is treated with ammonium molybdate reagent, ammonium silicomolybdate is formed, which on treatment with stannous chloride, is reduced to molybdenum blue. Ammonium molybdate, itself, is not reduced to molybdenum blue by stannous chloride.

Here also phosphate and arsenate can not interfere, as the test is conducted with the volatile SiF_4 , which is free from phosphate and arsenate. Borate if present, interferes by forming volatile

boron trifluoride (BF_3) along with SiF_4 . Borate should be removed by warming the sample with methanol and conc. H_2SO_4 in a Pt or Pb capsule before performing the silicon tetrafluoride test.

Mix a small amount ($\sim 0.1\text{g}$) of the solid sample or the silica residue obtained after extracting Na_2CO_3 fusion melt with HCl , with one third of its mass of sodium (or calcium) fluoride in a Pt or a Pb crucible, moisten the mixture with a few drops of conc. H_2SO_4 to form a thin paste. Mix with a stout Pt-wire, cover the crucible with its lid having a small hole in it. Warm gently in a **FUME CUPBOARD**. Hold a drop of $2N$ NaOH solution supported on a Pt-wire loop over the hole of the crucible lid, so that the drop of NaOH comes in contact with the issuing gas if any. Now transfer the drop into a spot plate, add 2-3 drop of 10% ammonium molybdate reagent and then a few drops of $4N$ acetic acid until faintly acidic. Add a few drops of 5% SnCl_2 in $3N$ HCl solution, finally drops of conc. NaOH solution ($\sim 5N$) until the precipitate of $\text{Sn}(\text{OH})_2$ that is initially formed, just dissolves in excess of alkali. A blue colouration results if silicate is present. Arsenate and phosphate do not interfere.

Note : Arsenate and phosphate will interfere, if the test is conducted with the solution of silicate.

Limit of dilution : 1 : 10,000.



CHAPTER - 6

Preliminary Dry Tests for Cation and Anion Radicals

6.1 Introduction

Qualitative inorganic analysis employs two types of experiments: (i) dry tests and (ii) wet reactions. Dry tests or preliminary tests, are carried out with solid samples or materials, whereas, for carrying out the wet reactions the substance under examination has to be transformed into solution by extracting with (i) water, (ii) dilute or concentrated acids, (iii) caustic alkali, (iv) sodium carbonate solution or (v) fusion with fusion-mixture followed by extraction with water and (vi) fusion with potassium pyrosulfate followed by extraction with dilute H_2SO_4 . Technical aspects for carrying out some of the important dry tests are discussed in this chapter.

Dry tests are carried out before dissolving the sample for wet analysis. Dry tests often provide valuable clues to the presence or absence of certain radicals. The course of the wet analysis may be organized/modified based upon the information obtained from dry tests. The course of the analysis may be shortened to a great extent by making use of the information obtained from the dry tests coupled with sound chemical knowledge. The course of the analysis may be very much complicated without any preliminary knowledge about the radicals, as may be obtained from dry tests.

6.2 Examination of Physical Nature : Colour and Texture

The physical appearance of the materials should be carefully examined with the help of a magnifying lens or a microscope if necessary. The following characteristics are to be noted and recorded,

- (i) Texture - crystalline or amorphous,
- (ii) Hygroscopic or deliquescent,
- (iii) Whether attracted by a magnet (i.e. whether magnetic),
- (iv) Whether possesses any characteristic odour,
- (v) Whether coloured or white.

Alkali metal (Na^+ , K^+) and NH_4^+ salts are mostly crystalline. Sulfate, nitrate, halide salts of transition and post-transition metals are also crystalline and often contain water of crystallization. Oxides, carbonates and sulfides of most metals are amorphous.

Alkali and alkaline earth metal compounds are white coloured. Transition metal compounds occur in different colours. Post-transition metal salts are mostly white coloured, but those with heavier anions (S^{2-} , Br^- , I^-) and oxides are coloured. Some commonly occurring coloured compounds are listed here :

Black : PbS , HgS , CuS , FeS , CoS , NiS , Ag_2S ;
 CuO , MnO_2 , Co_3O_4 , $Pb_2S_2O_3$.

- Brown:** PbO_2 , CdO , Fe_3O_4 , Ag_3AsO_4 , SnS , Bi_2S_3 , MnS , $\text{Fe}(\text{OH})_3$ and Fe_2O_3 (red-brown) [MoO_2 , UO_2]*
- Blue:** $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, other hydrated Cu^{II} -salts, Prussian blue, anhydrous Co^{II} -salts. [V^{IV} , VO^{2+} (vanadyl), Mo_2O_5 , 2MoO_3 , W_2O_5]*
- Green:** Hydrated Fe^{II} -salts, eg. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4 \cdot \text{FeSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, CuCO_3 , Cr_2O_3 , $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Cr}(\text{OH})_3$, K_2MnO_4 , Hg_2I_2 ; hydrated Ni^{II} salts, e.g. $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$. [V^{III} , phosphomolybdic acid, U_3O_8 , U^{IV} compounds]*
- Yellow:** Chromates of alkali, alkaline earth metals: K_2CrO_4 , Na_2CrO_4 , CaCrO_4 , SrCrO_4 , BaCrO_4 , PbCrO_4 ; CdS , As_2S_3 , As_2S_5 , SnS_2 ; PbI_2 , HgO (precipitated), Fe^{III} salts eg. FePO_4 , FeCl_3 , $\text{K}_4[\text{Fe}(\text{CN})_6]$; [Ce^{IV} -salts, uranyl salts, phosphomolybdates, WO_3 , UO_3]*.
- Orange:** Sb_2S_3 and Sb_2S_5 (orange-red), $\text{K}_3[\text{Fe}(\text{CN})_6]$, $\text{K}_2\text{Cr}_2\text{O}_7$, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, Ag_2CrO_4 .
- Pink :** Hydrated salts of Co^{II} and Mn^{II} , permanganate (KMnO_4), Cr^{III} alums,
- Red :** Pb_3O_4 , CrO_3 , Cu_2O , Fe_2O_3 , HgO , HgI_2 , As_2S_2 , $\text{Cu}_2[\text{HgI}_4]$.
- White :** BaSO_4 , SrSO_4 , CaSO_4 , PbSO_4 , Al_2O_3 , carbonates, silicates of Ba, Sr, Ca, Pb, Cd, Mg; $\text{SiO}_2 \cdot x\text{H}_2\text{O}$; sodium, potassium and ammonium salts with non-metallo acids. [Be^{II} , Zr^{IV} , Th^{IV} , Ti^{IV} compounds, MoO_3]*

6.3 Ignition Test

Take a small amount (<0.1g) of the solid sample in a dry test tube (60-70 mm $\times$ 7-8 mm) plug the mouth of the test tube with a small piece of cotton wool, heat first gently and then strongly by holding the test tube slightly tilted over a non-luminous Bunsen flame and observe if the following changes take place :

(i) *Change of colour :*

Due to decomposition and also due to loss of water of crystallization.

(ii) *Evolution of gases :*

Due to decomposition of salts eg, nitrate, nitrite, bromide, iodide, carbonate, bicarbonate, sulfide, sulfite, thiosulfate etc. Ammonia is evolved when ammonium salts are heated in presence of basic substances and alkalies.

(iii) *Formation of sublimate :*

Vapour evolved on heating the sample, condenses and deposits as solids on the cooler part of the test tube. Sublimates are mainly formed by mercury, arsenic and ammonium salts. The colour of the sublimate gives important clues for identification of radicals.

Observations on ignition tests with some known substance are listed below.

*Rare elements

(i) Evolution of gaseous product and (ii) Change of colour etc.

Sl. No.	Substance	Observations
1.	Carbonate, bicarbonate	Decomposition, evolution of CO_2 , turns lime-water turbid (<i>cf.</i> Fig. 3.31) $\text{MgCO}_3 \rightarrow \text{MgO} + \text{CO}_2 \uparrow$ $\text{CO}_2 + \text{Ca(OH)}_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O}$
2.	Nitrate, nitrites of heavy metals	Dark brown or redish fume (of oxides of N), acidic reaction to moist litmus paper (<i>cf.</i> Fig. 3.27) $2\text{Pb(NO}_3)_2 \rightarrow 2\text{PbO} + 4\text{NO}_2 \uparrow + \text{O}_2 \uparrow$ $2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_3 + \text{HNO}_2$
3.	Compounds with water of crystallization, hydroxides, acid salts, NH_4^+ salts	Evolution of water vapour, condensing at the cooler part of the test tube, often change of colour (for transition metal salts), some times change of litmus colour (<i>cf.</i> Fig. 3.27) $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} \rightarrow \text{CuSO}_4 + 5\text{H}_2\text{O} \uparrow$ <i>(blue)</i> <i>(white)</i> $2\text{CuSO}_4 \rightarrow 2\text{CuO} + 2\text{SO}_2 \uparrow + \text{O}_2 \uparrow$ <i>(white)</i> <i>(black)</i>
4.	Ammonium salts, such as $(\text{NH}_4)_2\text{CO}_3$	Evolution of ammonia, turns red litmus paper blue (<i>cf.</i> Fig. 3.27)
5.	Ammonium nitrate	Evolution of nitrous oxide and steam, with rekindling of glowing splint $\text{NH}_4\text{NO}_3 \rightarrow \text{N}_2\text{O} \uparrow + 2\text{H}_2\text{O} \uparrow$
6.	Sulfite, thiosulfate and certain sulfates	Evolution of SO_2 , decolourises fuchsin solution, turns acid $\text{K}_2\text{Cr}_2\text{O}_7$ paper green (<i>cf.</i> Fig. 3.29)
7.	Hydrated sulfide	Evolution of H_2S , turns Pb-acetate paper black (<i>cf.</i> Figs. 3.2 and 3.29).
8.	Unstable chloride salts or chloride in presence of oxidizing agents	Evolution of yellowish-green (Cl_2) gas, bleaches moist litmus paper, turns starch iodide paper blue. [Caution : don't inhale] (<i>cf.</i> Fig. 3.29).
9.	Bromide in presence of oxidizing agents	Redish-brown (Br_2) vapour, turns starch-iodide paper blue, turns fluorescein paper red. (<i>cf.</i> Fig. 3.27).
10.	Iodide salts	Violet (I_2) vapour, condensing to black crystals, turns starch paper blue (<i>cf.</i> Fig. 3.27).

Sl. No.	Substance	Observations
11.	Alkali metal salts [NaCl, KCl, K_2SO_4 , $KHSO_4$ etc.]	Melting occurs.
12.	Zinc salts	Yellow when hot white when cold.
13.	Pb-compounds	Yellow when hot and cold.
14.	Ammonium dichromate (CAUTION)	Vigorous reaction with firing, evolution of colourless odour less (N_2) gas, change of colour from redish brown, $(NH_4)_2Cr_2O_7$ to green Cr_2O_3 . $(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2\uparrow + 4H_2O\uparrow$

(iii) Formation of Sublimate (Caution: Poisonous)

Sl. No.	Samples	Observations
1.	Ammonium salts, Hg(II) salts, As_2O_3 , Sb_2O_3	White sublimate.
2.	As_2S_3 , HgI_2	Yellow sublimate.
3.	Hg-salts	Grey sublimate, easily rubbed to globules of mercury.
4.	As-compounds	Steel grey sublimate.

If a sublimate is formed, mix a small amount ($<0.1g$) of the sample with 4 times its bulk of anhydrous sodium carbonate and a small amount of charcoal powder. Place the mixture in a dry test tube, plug the mouth of the test tube with small piece of cotton wool (*cf.* Fig. 3.27) heat the mixture with a non-luminous flame of the burner and note the observations:

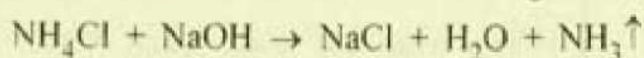
Sl. No.	Samples	Observations
1.	Hg-compounds (POISONOUS)	Grey mirror, transforms into globules of Hg on rubbing with a glass rod.
2.	As-compounds (POISONOUS)	Browish black mirror with white sublimate.
3.	NH_4^+ salts	Evolution of ammonia, turns moist red litmus paper blue, mercurous nitrate paper black (<i>cf.</i> Fig. 3.27).

6.4 Action of Caustic Alkali (Test for NH_4^+ radical)

If ammonium radical is suspected in the ignition test (i.e. if a white sublimate is formed), perform the following test).

Take a small amount ($< 0.1g$) of the sample in a semi-micro test tube and add cautiously $\sim 0.5\text{ ml}$ of strong ($\sim 5M$) sodium hydroxide solution using a dropper. Plug the mouth of the

test tube with piece of clean cotton wool (cf. Figs. 3.27, 3.29) and heat the mixture gently. Hold a drop reaction paper spotted with phenolphthalin indicator to the issuing gas. A red spot appears, which disappears on drying the paper, indicating the presence of ammonium radical. Ammonium salts react with caustic alkali to set free ammonia, which turns phenolphthalin red. On drying the paper, ammonia volatilizes out, turning the indicator paper colourless.



Note : Care should be taken to avoid contamination of NaOH solution with the drop reaction paper. If the paper is contaminated with NaOH solution, phenolphthalin turns permanently red. The red colour does not disappear on drying the paper.

6.5 Flame Test

Compounds of certain metallic elements when exposed to the non-luminous flame of a Bunsen burner, impart characteristic colours to the flame. Since chloride salts of metals are among the most volatile metallic compounds, these are generated *in situ* by moistening the solid sample with a little conc. HCl while applying the flame test.

To understand the physicochemical aspects of the flame test it is essential to have some preliminary knowledge about the structure and chemical characteristics of a non-luminous Bunsen flame, which consists of the several parts (Fig. 6.1).

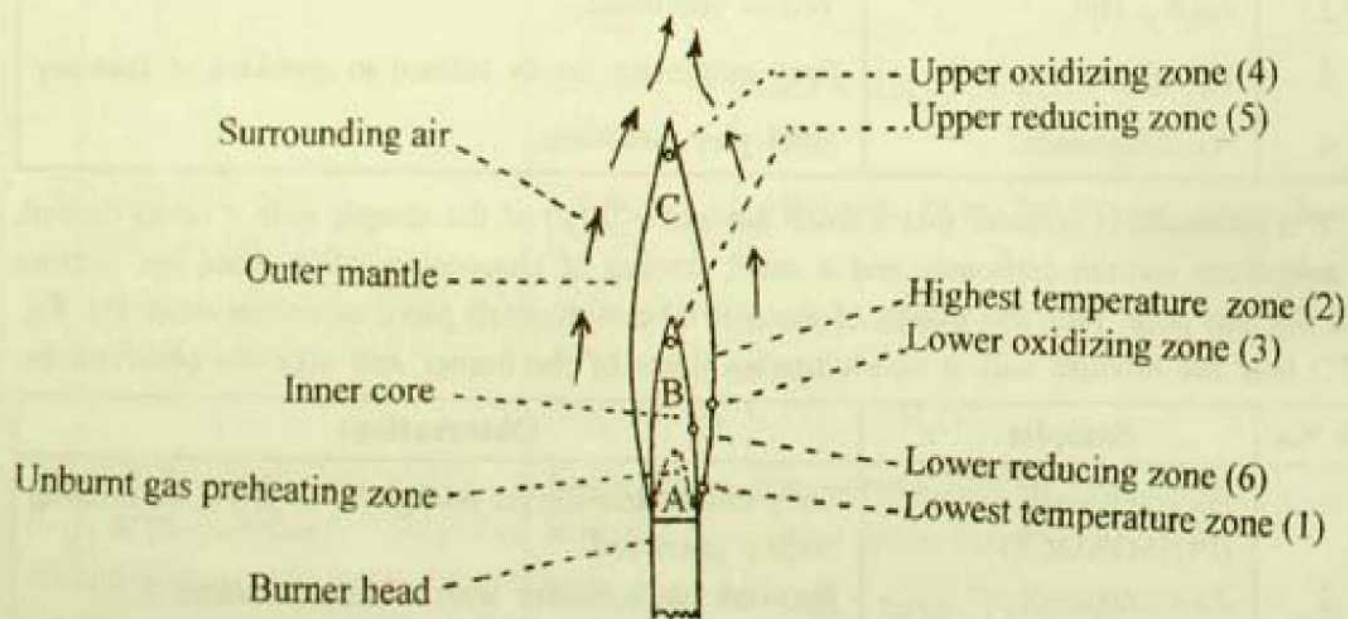


Fig.6.1. Structure and chemical nature of different zones of non luminous Bunsen flame.

- (i) inner blue zone-A consisting of unburnt fuel gases,
- (ii) a luminous part-B, visible when the air hole is slightly closed,
- (iii) an outer mantle-C, where complete combustion of fuel gases takes place.

The gas in zone-A is preheated by conduction and radiation from the reaction zone-B and by diffusion of radicals into it. The gases emerging from zone-B consist mainly of CO, H₂, CO₂ and H₂O (vapour) and N₂ (if air is one of the original gas), with small amounts of H,

O and OH. The actual composition of the gas mixture of course, depends upon the initial composition of the fuel, proportion of air in the mixture and temperature. The gases in this region are not in thermal equilibrium. The proportions of the free radicals are very large and these serve as precursors of chemi-luminescent reactions. The outer mantle (region-C) has the highest temperature and the gases in this region are at complete thermal equilibrium.

The lowest temperature zone (1) is located at the base of the flame. This zone is employed for testing of flame colouration with volatile materials. The hottest part of the flame is the fusion zone (2), occurring about one third of the height of the flame, nearly equidistant from the inside and outside of the mantle. This region is employed for examining the fusibility of materials. Just outside border of this hottest zone (2), is situated the lower oxidizing zone (3), which is employed for oxidation of substances fused in borax beads, microcosmic salt beads or sodium carbonate beads. The upper oxidizing zone (4) is situated on the top of the non-luminous flame. Although oxygen supply is plenty in this region, but the temperature is not as high as in the lower oxidizing zone (3). This region may be employed for oxidation processes, which do not require the highest temperature. At the tip of the inner blue cone (B), is situated the upper reducing zone (5), which is rich in incandescent carbon and is suitable for reduction reactions, particularly of metallic oxides to the metals. Inside the inner edge of the mantle, next to the blue cone, is situated the lower reducing zone (6). In this region, the reducing fuel gases mix with O_2 (air). Reducing power of this region is lower than that of the upper reducing zone (5). This region is suitable for reduction of substances fused in borax or microcosmic salt or sodium carbonate beads.

Procedure of flame test

Platinum wire: A thin platinum wire (diameter ~ 0.05 mm, length $\sim 3-5$ cm) is fused into the end of a short piece of ($\sim 10-15$ cm) glass rod or glass tubing, which serves as the handle.

Cleaning of platinum wire

The platinum wire should be thoroughly cleaned before using it for flame test. For this purpose the wire should be first dipped into concentrated hydrochloric acid and taken in a small watch glass and heated in the fusion zone (2) of the non-luminous flame of a Bunsen burner. The operation should be repeated until no colour is imparted to the flame. Some times the platinum wire after use acquires a deposit, which is often difficult to remove by this simple treatment with concentrated hydrochloric acid and then heating. Such deposits may be conveniently removed by treatment with fused potassium hydrogen sulfate ($KHSO_4$) or borax ($Na_2B_4O_7 \cdot 10H_2O$). A coating of these salts may be made to adhere to the platinum wire, first by heating the wire to dull redness and then drawing the red hot wire across a crystal of these solid salts. If the wire, coated with these salts, is now passed slowly through the flame, a bead of the salt ($KHSO_4$ or borax) is formed and travels along the wire. This molten bead dissolves the contaminating deposits (mostly metallic oxides and salts) on the platinum wire.

NB : For the chemical reactions involved in this cleaning operation, see borax bead test and fusion test with KHSO_4 (cf. Sects. 6.6, 7.9c).

After a few run of the molten bead across the hot platinum wire, the bead is to be dislodged from the wire by taking it out of the flame, so that it is cooled some what and then jerking the glass rod gently. Any small residue of KHSO_4 or borax on the wire dissolves readily in water. For removing the last traces of these salts, the wire is moistend with concentrated hydrochloric acid and then heated in the flame as before repeately until it imparts no colour to the flame.

Flame testing with the sample

Dip the tip of the clean platinum wire into a fresh portion of concentrated hydrochloric acid taken in a watch glass, touch the powdered sample with the HCl-moisten wire so that a minute grain of the sample adheres to the wire. Introduce the wire with the sample at its head into the lower oxidizing zone (3) of the non-luminous Bunsen flame and observe the colour imparted to it. Repeat this operation of moistening the wire with conc. HCl and heating it in the lower oxidizing zone (3) first (for more volatile materials) and then in the fusion zone (2) (for less volatile substances) to identify the element imparting the colour to the flame. When more than one element produce mixed colouration to the flame, it is often possible to filter out one colour from the mixture by viewing the flame colour through two thickness of cobalt glass (double blue glass as are commonty called). As for example, sodium imparts bright golden yellow colour and potassium imparts violet (lilac) colour to the flame. The violet colour due to potassium is masked by the bright golden yellow colour due to sodium if the flame is viewed through naked eye. But when viewed through the double blue glasses, the yellow sodium flame colour is absorbed and the potassium flame colour appears crimson red.

Perform flame tests with salts of Na, K, Ca, Sr, Ba, Cu and record your observations.

Sl. No.	Samples (Salts/componds of)	Observations : Flame colouration
1.	Sodium	Persistent golden-yellow
2.	Potassium	Violet (lilac)
3.	Calcium	Transicent brick red (yellowish)
4.	Strontium	Crimson red
5.	Barium (Molybdenum) [#]	Yellowish green
6.	Copper, Borates	Green
7*.	Lead, Arsenic Antimony, Bismuth, also Coppers	Blue

* Platinum wire is corroded by lead, arsenic, antimony and bismuth compounds.

Rare element

If sodium, potassium, calcium, strontium and barium are suspected in the flame test, view the flame through double blue glasses and record your observations.

Sl. No.	Samples (Salts/Compounds)	Observations : Flame colouration	
		Through naked eye	Through double blue glasses
1.	Sodium	Golden yellow	Colourless
2.	Potassium	Violet (lilac)	Crimson red
3.	Calcium	Transient brick-red	Light green
4.	Strontium	Crimson	Purple
5.	Barium	Yellowish green	Yellowish green

After all the tests are completed, clean the platinum wire as described before and store the same in concentrated hydrochloric acid taken in hard glass test tube. For this purpose fix a cork with the glass rod at the end opposite to that holding the platinum wire. Fit the glass rod at the mouth of the hard glass test tube with the help of this cork. Half fill the test tube with concentrated hydrochloric acid so that the full length of the platinum wire remains immersed into the acid.

Chemistry of flame colouration

The following sequence of events take place rapidly when a platinum wire containing the sample, moistened with concentrated hydrochloric acid (for transformation into chloride salts *in situ* for their higher volatility), is heated in a non-luminous flame of a Bunsen burner.

(i) Water and hydrochloric acid are vaporised leaving minute particles of the dry salt (chlorides).

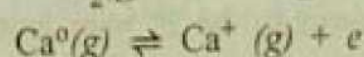
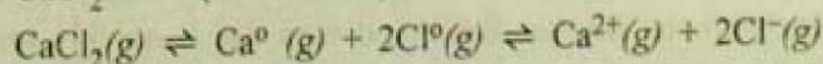
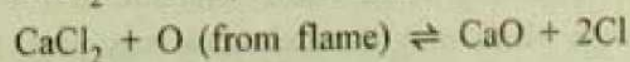
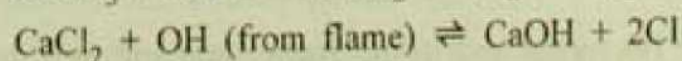
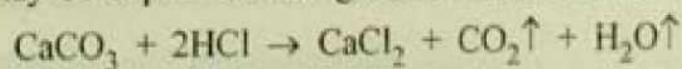
(ii) The dry salt is vaporised at the high temperature of the flame, and part or all of the gaseous molecules progressively dissociate to give neutral atoms.

(iii) Some of the free metal atoms react with the other atoms and radicals present in the flame gas.

(iv) The vapours of the neutral metal atoms or of the molecules containing the metal atoms are excited by the thermal energy of the flame, or by any chemical excitation mechanism. Ionization and excitation of the neutral atoms may also take place to some extent.

(v) From the excited electronic states, the atoms, molecules and the ions then relax or return to their respective ground electronic states partly by impacts with other species and partly by spontaneous emission of radiations that fall in the visible region.

The process may be explained taking calcium chloride or calcium carbonate as example:

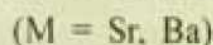
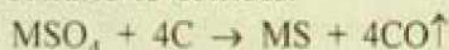


The excitation process raises the energy of the electrons in the atoms/molecules/ions to higher energy levels (E_2) and this is followed by loss of a discrete amount of energy in the form of radiant energy ($E_2 - E_1 = \Delta E = h\nu$) as the electron falls back into its original position or a lower energy level (E_1). In neutral atom spectra, the emission of radiation occurs as discrete lines, not necessarily of single wave length. The electrons may relax to the ground state through a series of intermediate energy levels, emitting several spectral lines.

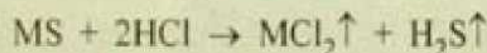
Each period of the periodic table starts with an alkali metal, for which the differentiating electron occupies a higher quantum shell and this is followed by an alkaline earth metal, the new electron of which also occupies the same quantum shell. The attraction of the positive nucleus for the outer most electrons of the alkali and alkaline earth metals atoms are relatively weaker than those in the case of the p -block elements of the same period, in which the outermost electron shells are drawn closer to the nucleus with increase of nuclear charge, as the differentiating electrons are added to the same p -subshell. For this reason, the outer most electrons of the alkali and alkaline earth metals may be promoted to higher energy levels by excitation with even relatively lower energy as available from an ordinary fuel gas Bunsen flame, with which it is not possible to excite the outermost electrons of the p -block elements. The d -block metal copper is, however, similar to the alkali/alkaline earth metals in this respect and responds to flame test.

Special procedure for flame test with insoluble sulfates : (SrSO_4 , BaSO_4)

Sulfates of strontium and barium are insoluble in concentrated hydrochloric acid. As such these are not transformed to the corresponding chlorides when moistened with concentrated hydrochloric acid, as is done before flame test. However, these sulfates may be reduced to sulfide by heating the HCl-moistened sample at the tip of the platinum wire in the upper reducing zone (5) of the non-luminous Bunsen flame. This zone is rich in incandescent carbon particles, which reduce the sulfates to sulfides.



When the sulfide incrustation (MS) on the platinum wire is brought into contact with concentrated hydrochloric acid, the sulfides dissolve in HCl to produce the metallic chlorides.

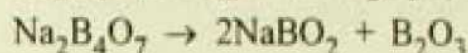
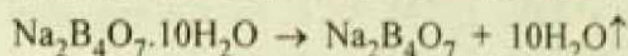


The platinum wire is now heated in the lower oxidizing zone (3) of the non-luminous Bunsen flame. If this operation is repeated 2-3 times, the characteristic colour of the flame then appears.

6.6 Borax Bead Test

Take a clean platinum wire (as mentioned in the flame test) and coil its free end into a small loop ($\sim 2 \text{ mm}$ diameter) through which only a match stick may pass. Heat the loop to dull redness in the non-luminous Bunsen flame and then dip it quickly into borax powder ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$). Small amount of solid borax adheres to the Pt wire loop. Now hold the

wire in the hottest part of the flame. The salt swells up as it loses its water of crystallization, eventually it shrinks and forms a colourless glass like transparent bead on the loop. The chemical composition of this borax bead is a mixture of sodium metaborate (NaBO_2) and boric anhydride (B_2O_3), formed due to thermal dehydration of borax followed by thermal decomposition :



Now dip the bead, while still hot, into the finely powdered sample to be tested, so that a minute grain of the sample adheres to the bead.

NB : Only minute quantity of the substance should adhere to the bead. Otherwise, the bead may become dark and opaque in the heating operation that follows.

Now heat the bead containing the sample first in the lower reducing zone (6) of the non-luminous Bunsen flame, allow to cool and observe the colour. Next, heat the bead in the lower oxidizing zone (3) of the flame, allow cool and observe the colour again. Characteristic coloured beads for heating in the oxidizing and in the reducing flames are observed with transition metal compounds i.e. with Cu, Fe, Cr, Mn, Co, Ni salts (also with the rare elements Mo, Au, W, U, V, Ti, Ce).

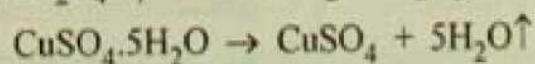
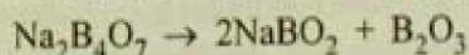
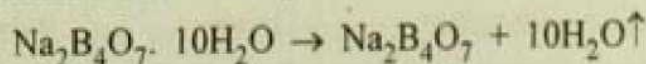
After each individual test, the borax bead has to be removed from the platinum wire. For this purpose, heat the bead again in the hottest part of the non-luminous Bunsen flame so that the bead melts. Give a gentle jerk to the glass handle, the bead is dislodged. Dip the red hot wire again in some borax powder and heat the adhering borax again until another borax bead is formed, then dislodge the bead as before. Repeat this operation 2-3 times so that the last trace of the sample is removed from the wire. Then moisten the wire with concentrated hydrochloric acid taken in a watch glass and heat the HCl-moistened wire in the hottest part of the non-luminous flame. Repeat this operation until the flame does not show any golden yellow colouration (due to sodium from borax).

Chemistry of borax bead test

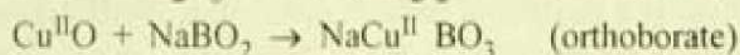
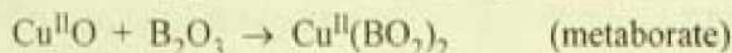
The colours of the borax beads are due to coloured borate salts (or complexes) formed by transition metals, which because of their ability to exist in more than one easily inter convertible oxidation states, give borates of different colours when heated in oxidizing and reducing flames. Compounds of coinage metals (eg. Cu) may even be reduced to elemental state when its borate bead is heated in the reducing flame.

The chemical reactions involved in borax bead test will be illustrated here with a copper (II) salt, eg, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

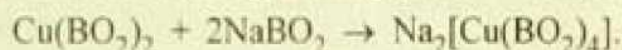
Thermal dehydration and decomposition reactions:



Reactions in the oxidizing flame : Formation of Cu(II) borates :

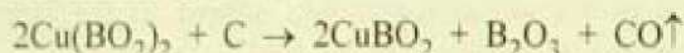


Complex meta borates, eg, $\text{Na}_2[\text{M}(\text{BO}_2)_4]$, $\text{M} = \text{Co}, \text{Ni}, \text{Cu}$ may also be formed :

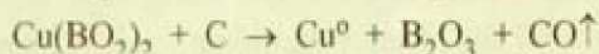


Reactions in the reducing flame :

(i) Reduction of blue coloured Cu(II) borates to colourless Cu(I) borates by the incandescent carbon present in the reducing flame,



(ii) Reduction of blue coloured Cu(II) borate to opaque-red coloured metallic copper (Cu) by incandescent carbon present in the reducing flame,



With iron salts, ferric metaborate $\text{Fe}(\text{BO}_2)_3$ and ferrous metaborate $\text{Fe}(\text{BO}_2)_2$ are formed in oxidizing and reducing flames respectively.

Colours of borax beads

(i) *With 3d transition metal compounds*

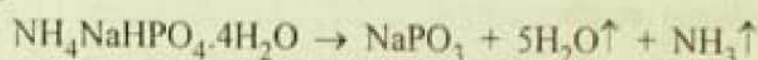
Sl. No.	Metal	Oxidizing flame		Reducing flame	
		Hot	Cold	Hot	Cold
1.	Copper	Green	Blue	Colourless	Opaque red-brown
2.	Cobalt	Blue	Blue	Blue	Blue
3.	Chromium	Yellow	Green	Green	Green
4.	Manganese	Violet (amethyst)	Amethyst	Colourless	Colourless
5.	Iron	Yellow-brown	Yellow	Bottle-green	Bottle-green
6.	Nickel	Violet	Redish-brown	Grey	Grey

(ii) *With compounds of rare elements*

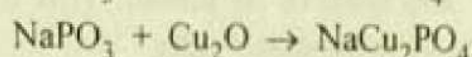
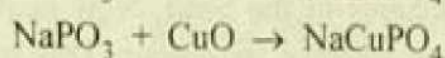
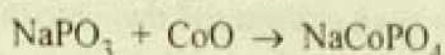
Sl. No.	Metal	Oxidizing flame		Reducing flame	
		Hot	Cold	Hot	Cold
1.	Molybdenum	Yellow	Colourless	Brown	Brown
2.	Tungsten	Yellow	Colourless	Yellow	Yellow-brown
3.	Uranium	Yellow	Pate-yellow	Green	Bottle-green
4.	Titanium	Yellow	Colourless	Green	Pale-violet
5.	Vanadium	Yellow	Greenish-yellow	Brownish	Emerald-green
6.	Cerium	Orange-red	Colourless	Colourless	Colourless
7.	Gold	Rose-violet	Rose-violet	Red	Violet

6.7 Microcosmic Salt (Phosphate) Bead Test

Microcosmic salt is ammonium sodium hydrogenphosphate tetrahydrate, $\text{NH}_4\text{NaHPO}_4 \cdot 4\text{H}_2\text{O}$. On heating in the non-luminous Bunsen flame, the salt undergoes thermal dehydration and deammoniation to produce colourless transparent mass of sodium metaphosphate (NaPO_3).



A sodium metaphosphate bead can be formed on a clean platinum wire loop in the same manner as the borax bead described before (*cf.* Sect. 6.6). The molten metaphosphate bead combines with oxides and other salts of transition metals to form orthophosphates, which are coloured and are often different coloured when heated in oxidizing and reducing flames and observed in hot and cold conditions.



Colours of microcosmic salt beads

(i) With 3d transition on metal compounds

Sl. No.	Metal	Oxidizing flame		Reducing flame	
		Hot	Cold	Hot	Cold
1.	Copper	Green	Blue	Colourless	Red
2.	Cobalt	Blue	Blue	Blue	Blue
3.	Chromium	Green	Green	Green	Green
4.	Manganese	Violet	Violet	Colourless	Colourless
5.	Iron	Yellow (yellow-brown)	Yellow	Yellow	Colourless/bottle green
6.	Nickel	Brown	Brown	—	Grey

(ii) With rare element compounds

Sl. No.	Metal	Oxidizing flame		Reducing flame	
		Hot	Cold	Hot	Cold
1.	Titanium	Colourless	Colourless	Yellow	Violet
2.	Vanadium	Yellow	Yellow	—	Green
3.	Uranium	Yellow	Yellow-green	Green	Green
4.	Tungsten	Pale yellow	Colourless	Green	Blue

Acidic oxides such as silica (SiO_2) do not dissolve in molten phosphate bead. If silicate salts are strongly heated on a microcosmic salt bead, silica is liberated (since silicic acid is weaker than phosphoric acid) and floats on the molten bead in the form of a semi-translucent mass, which can be seen during and after fusion.



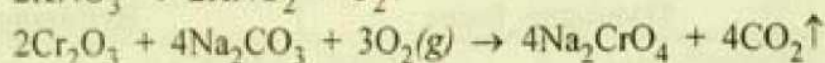
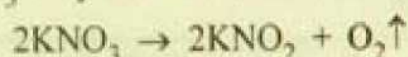
This reaction offers a test for detection of silicate salts and silica or silicic acid. But this can not be a confirmatory test for silica or silicate since some metallic silicates dissolve in phosphate bead.

Borax beads being more viscous than phosphate beads, adhere to the platinum wire much better, but colours of the metallic phosphate beads, although similar, but are more pronounced than the corresponding borax beads.

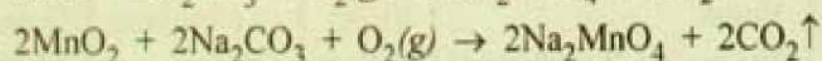
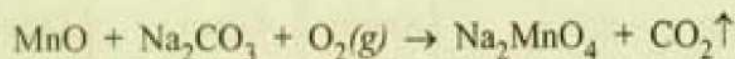
6.8. Oxidative Fusion Test on Sodium Carbonate Bead

On a clean platinum wire loop, form a sodium carbonate bead in the same manner as the borax bead or microcosmic salt bead, by heating the anhydrous salt on the platinum wire loop strongly on a non-luminous Bunsen flame. Unlike borax and phosphate beads which are transparent, the sodium carbonate bead is opaque. Moisten the bead slightly and dip it into a little potassium nitrate (KNO_3) which serves as an oxidant and then into the powdered sample, so that a minute grain of the solid sample adheres to the bead. Now heat the whole bead in the oxidizing flame of the Bunsen burner and observe its colour. This oxidative fusion test is very useful for detection of chromium and manganese salts.

Chromium salts are first transformed to green chromic oxide (Cr_2O_3), which is subsequently oxidized by KNO_3 to yellow coloured chromate (CrO_4^{2-}) ion :



Manganese salts are first transformed to manganese oxide (MnO) or black manganese dioxide (MnO_2), which are subsequently oxidized by KNO_3 to green coloured manganate (MnO_4^{2-}) ion :



Treatment of coloured sodium carbonate beads

Dissolve the yellow or green coloured sodium carbonate bead in 2-3 drops of water in a cavity of a spot plate and perform the following tests for chromium and manganese. If chromium is present, the colour of the bead as well as its aqueous extract will be yellow.

Place a drop of the yellow extract in another cavity of the spot plate, acidify with drops of acetic acid and then add a drop of lead acetate solution. Yellow precipitate lead chromate (PbCrO_4) appears. Perform other tests of chromate with the remaining amount of the yellow chromate extract (cf. Sect. 5.18).

If manganese is present, the colour of the bead as well as its aqueous extract will be green. Place a drop of the green extract in another cavity of the spot plate, acidify with drops of dilute HNO_3 and add a minute grain of sodium bismuthate (NaBiO_3) powder. Pink colouration appears as green coloured manganate (MnO_4^{2-}) is oxidized by sodium bismuthate to permanganate (MnO_4^-) ion.

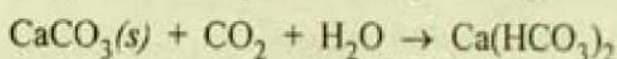
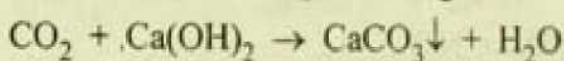
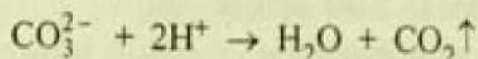


Note : The oxidative fusion test may also be carried out on a mica foil.

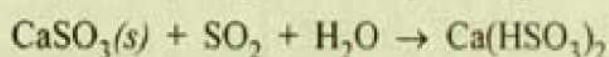
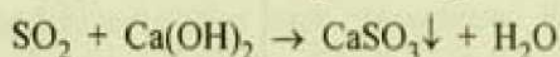
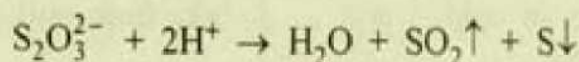
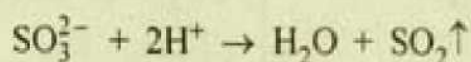
6.9. Action of Dilute Sulfuric Acid

Take a small amount (~ 10 mg) of the solid sample in a semi-micro test tube and add ~ 0.5 -1 ml of dilute 2N sulfuric acid, plug the mouth of the test tube with a piece of clean cotton wool (Fig. 3.27) and observe whether any chemical reaction takes place in the cold. Place the test tube on a hot water bath (Fig. 3.15) and observe any change that takes place.

Dilute sulfuric acid (dilute HCl may also be used) apart from dissolving the basic substances such as metallic oxides and hydroxides, decomposes the salts of weak acids such as carbonate, bicarbonate, sulfite, sulfide, thiosulfate, nitrite etc. Carbonates and bicarbonates decompose with evolution of colourless, odourless CO_2 gas, that turns lime-water turbid due to precipitation of CaCO_3 , which dissolves forming bicarbonate, on passing excess of CO_2 gas (cf. Fig. 3.31).



Sulfites and thiosulfates decompose with evolution of SO_2 gas having suffocating smell of burning sulfur [CAUTION : don't inhale]. Like CO_2 gas, SO_2 gas also turns lime-water turbid due to precipitation of CaSO_3 , which dissolves in excess of SO_2 , forming bisulfite (cf. Fig. 3.31). With thiosulfate salts, evolution of SO_2 is accompanied by separation of sulfur.



Because of reducing property, SO_2 gas

(i) discharges the blue colour of starch-iodine paper,



(ii) turns orange coloured acid dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) paper green due to Cr^{3+}

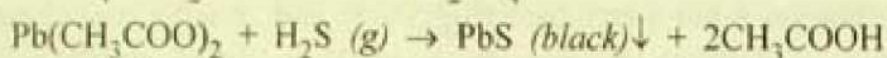


(iii) decolourises fuchsin paper (cf. tests for sulfite, Sect. 5.5).

Perform these tests in an apparatus as shown in Fig. 3.29.

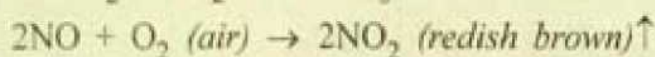
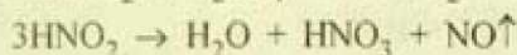
Sulfides of alkali and alkaline earth metals dissolve in dilute sulfuric acid with evolution of colourless H_2S gas having smell of rotten eggs [CAUTION : H_2S gas is **POISONOUS** don't inhale]. Sulfides of some earlier d -block elements dissolve in dilute H_2SO_4 with evolution of H_2S gas, but those of latter d -block elements do not. As for example, FeS dissolves in dilute H_2SO_4 with evolution of H_2S (cf. Sect. 3.3 Kipp's apparatus), whereas, CuS does not react with dilute H_2SO_4 . Rather, CuS is precipitated when Cu^{II} salt solutions are treated with H_2S

in acid medium. H_2S gas may be detected from blackening of lead acetate paper, held at the mouth of the test tube (cf. Fig. 3.27).



Note : Although both $\text{Fe}^{2+} (\text{aq})$ and $\text{Cu}^{2+} (\text{aq})$ ions are *borderline Lewis acids*, but in presence of a strong field *soft Lewis base* ligand, such as sulfide ion, Fe^{2+} assumes low spin configuration, and its radius becomes much smaller than that of Cu^{2+} ion under the same condition. As a result, Fe^{2+} behaves as a *hard Lewis acid*, showing reluctance to bind sulfide ion, whereas, Cu^{2+} behaves as a *soft Lewis acid*, prefers to bind sulfide ion.

Nitrite salts react with dilute H_2SO_4 with evolution of redish brown nitrous fumes,



Observations on treatment of same inorganic salts with dilute sulfuric acid are summarized below.

Sl.	Observations	Inference/Radicals
1.	Evolution of colourless odourless gas in cold, turning lime-water turbid.	CO_2 from carbonate/bicarbonates
2.	Evolution of colourless gas in cold with smell of burning sulfur, (i) turns lime-water turbid, (ii) discharges blue colour of starch - I_2 paper, (iii) turns acid dichromate paper green.	SO_2 from sulfite/bisulfite
3.	Evolution of SO_2 gas as in (2) with deposition of sulfur.	SO_2 gas from thiosulfate
4.	Evolution of SO_2 gas as in (2) on boiling	Thiocyanate
5.	Evolution of redish brown fumes in cold with disagreeable odour.	NO_2 from nitrite
6.	Evolution of colourless gas with smell of rotten eggs. (i) blackens lead acetate paper, (ii) cadmium hydroxide slurry turns yellow.	H_2S from sulfide.

6.10. Actions of Concentrated Sulfuric Acid

(a) Concentrated sulfuric acid alone

Take ~ 10 mg of the solid sample in a dry semi-micro test tube, add carefully a few drops (< 0.5 ml) of concentrated sulfuric acid using a dropper avoiding contact with the wall of the

tube. Plug the mouth of the test tube with a piece of pure cotton wool or fine glass wool (Fig. 3.27). Observe whether any reaction takes place in the cold. If no reaction takes place in the cold, place the test tube on a hot water bath (Fig. 3.15).

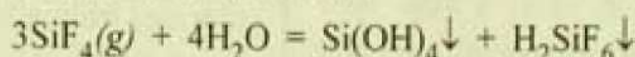
Concentrated sulfuric acid exerts dehydrating action in the cold and dehydrating as well as displacement reactions in the hot condition. Hot concentrated sulfuric acid may also exert oxidizing actions on easily oxidizable radicals, such as bromide and iodide.

All substance that react with dilute sulfuric acid, react vigorously with conc. H_2SO_4 involving rapid evolution of gaseous products.

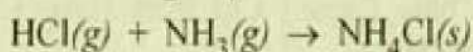
Concentrated sulfuric acid reacts with halide salts (MX) to liberate halogen acids (HX), X = halogen. HF gas attacks glass, forms oily bubbles sticking to the wall of the test tube as it reacts with silica of the glass to form silicon tetrafluoride gas.



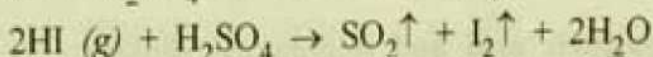
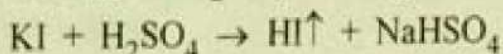
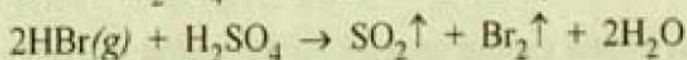
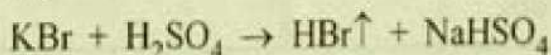
If the SiF_4 gas is brought into contact with water, gelatinous precipitate consisting of silicic acid and hexafluorosilicic acid is formed.



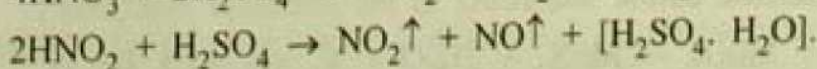
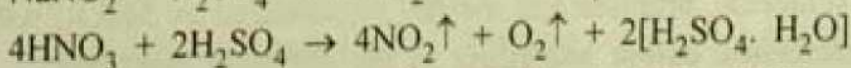
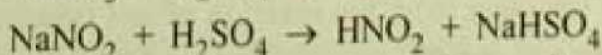
Concentrated sulfuric acid reacts with chloride salts, displaces colourless pungent smelling hydrogen chloride (HCl) gas, which forms white fume of NH_4Cl when brought into contact with ammonia gas.



Bromide and iodide salts react with concentrated sulfuric acid with evolution of pungent smelling hydrogen bromide (HBr) and hydrogen iodide (HI) gases, which are immediately oxidized by hot concentrated sulfuric acid, evolving brown vapour of bromine and violet vapour of iodine respectively.



Nitrate and nitrite salts react with conc. H_2SO_4 with displacement of the corresponding acids, which are immediately dehydrated by hot concentrated H_2SO_4 , when pungent smelling brown fumes composed of NO_2 , NO , O_2 appear according to reactions :



The observations and the inferences with different radicals are summarized below :

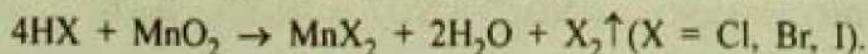
Sl.	Observations	Inference/Radicals
1.	Oily bubbles appear in the cold, the bubbles tend to adhere to the wall of the test tube and corrode glass. Gelatinous solid mass is formed if a drop of water is held to the issuing gas with the aid of a glass rod.	HF from fluoride
2.	Colourless gas of pungent odour. Fumes in air (i.e. in contact with moisture). Dense white fume (of NH_4Cl) appears when a drop of ammonia solution is held to the issuing gas with the aid of a glass rod.	HCl from chlorides
3.	Redish brown vapour of pungent odour, fumes in contact with moisture (air). Perform the same test in presence of (i) MnO_2 and (ii) Cu-turnings to differentiate (see latter).	HBr, Br_2 from bromides, NO_2 from nitrate, nitrite; CrO_2Cl_2 (chromyl chloride) from a mixture of chloride and chromate/ dichromate.
4.	Violet vapour with pungent odour.	HI and I_2 from iodides.
5.	Colourless gas evolved, burns with blue flame [CAUTION : Don't inhale, POISONOUS].	CO from ferrocyanide/ferricyanide
6.	Yellow colouration in cold, vigorous reaction occurs on warming. Evolved gas burns with blue flame (COS), decolourizes fuchsin solution (SO_2), separation of sulfur occurs.	COS and SO_2 from thiocyanate.

If a colourless or a redish brown vapour appears by the action of conc. H_2SO_4 (test 6.10a), perform the following tests.

(b) Action of concentrated sulfuric acid and manganese dioxide

Mix a small amount ($\sim 10 \text{ mg}$) of the solid sample and nearly the same amount of manganese dioxide in a dry semi-micro test tube, and add $\sim 0.5 \text{ ml}$ of conc. H_2SO_4 . Plug the mouth of the test tube with a piece of clean cotton wool or fine glass wool (*cf.* Fig. 3.29) and heat the mixture gently on a hot water bath.

Hydrogen halides (except HF) liberated from the reaction of hot concentrated sulfuric acid with halide salts (chloride, bromide and iodide) are oxidized by MnO_2 , with liberation of free halogens of characteristic colour according to the chemical reactions :

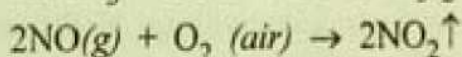
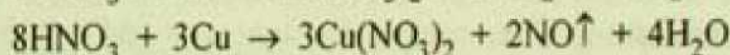
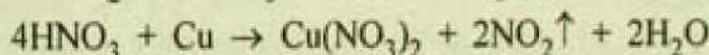
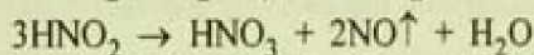


Sl.	Observations	Inference/Radicals
1.	Yellowish green gas evolved (i) irritating odour, (ii) bleaches litmus paper, (iii) turns KI-starch paper blue	Cl_2 from chloride
2.	Intense redish brown vapour evolved, turns (i) fluorescein paper red, (ii) fuchsin-bisulfite paper violet.	Br_2 from bromide
3.	Intense violet vapour evolved, colours starch-paper blue.	I_2 from iodide

(c) Action of hot conc. H_2SO_4 and copper turnings (Cu-T)

Mix a small quantity ($\sim 10 \text{ mg}$) of the solid sample with a few pieces of bright copper turnings in a semi-micro test tube and add a few drops ($< 0.5 \text{ ml}$) of conc. H_2SO_4 to it, using a dropper. Plug the mouth of the test tube with a piece of clean cotton wool or fine glass wool (*cf.* Fig. 329) and heat the mixture gently. Intense brown fume due to NO_2 appears and the resulting solution assumes a blue colour (due to Cu^{II}).

Nitrate and nitrite salts are ultimately transformed to nitric acid, that decomposes to produce brown fumes of NO_2 and reacts with metallic copper producing the $\text{Cu}(\text{II})$ nitrate :



6.11. Alkaline Reduction

Tests for Nitrate (or Nitrite) by reduction to NH_3

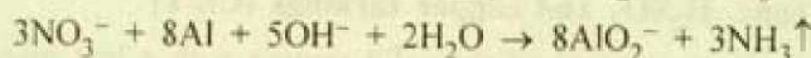
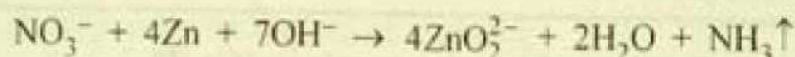
If NH_4^+ radical is suspected in the ignition test, it should be removed by boiling with caustic alkali before proceeding to this test.

(a) Take a small amount ($< 10 \text{ mg}$) of the solid sample in a semi-micro test tube, add $\sim 0.5\text{-}1 \text{ ml}$ of concentrated ($\sim 20\%$) sodium hydroxide solution carefully avoiding contact with the wall of the test tube, plug the mouth of the test tube with a piece of clean cotton wool (*cf.* Fig. 3.29) and heat the mixture gently. Hold a drop reaction paper spotted with a drop of phenolphthalin indicator to the issuing gas. If the spot turns red, ammonia is present. Now hold the paper near the flame. Red colour disappears as ammonia is evaporated. Retention of the red spot even on holding the paper near the flame indicates contamination with sodium

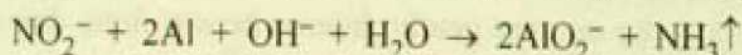
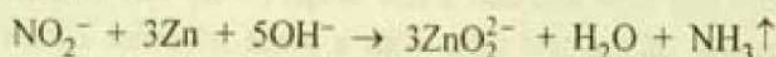
hydroxide. In that case, discard the paper and take a new one spotted with phenolphthalin indicator.

(b) If ammonia is present, continue boiling the sample with NaOH solution until ammonia is completely removed (indicated by no red colouration of phenolphthalin paper, test 6.11a). Cool the solution to room temperature and add a little (~ 0.1g) of zinc dust, or aluminium foil, or *Devarda's alloy* (Al 45%, Zn 5% and Cu 50%). Add a few drops of water if necessary and heat the mixture gently. Remove the test tube from the flame occasionally to reduce the vigour of the reaction due to evolution of hydrogen gas. Hold a filter paper spotted with phenolphthalin indicator to the issuing gas (Fig. 3.27). Appearance of red colour and its disappearance on drying the paper at this stage indicate nitrate/nitrite.

(i) *Reactions with nitrates :*



(ii) *Reactions with nitrites :*



Note : Thiocyanates, ferrocyanides, ferricyanides etc. may also respond to this test. So nitrate/nitrite indicated by this test, should be confirmed by their characteristic wet tests (*cf.* Sect. 4.24).

6.12. Chromyl Chloride Test for Chloride

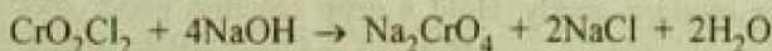
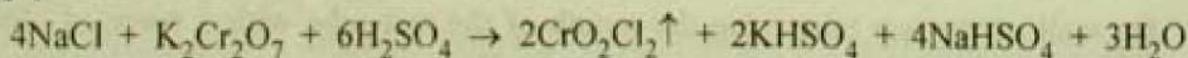
This test should be performed if halides are indicated by the aciton of concentrated sulfuric acid on the sample (test 6.10).

Mix a small quantity (< 0.1g) of the solid sample intimately with three times its bulk of powdered potassium dichromate in a semi-micro test tube and add 1-2 drops of concentrated sulfuric acid. Place a drop of dilute sodium hydroxide solution at the head of a glass knob or a capillary dropper above the mixture (Fig. 3.29b). Warm the mixture gently for a few minutes. The NaOH solution assumes a yellow colour if chloride (or fluoride) is present. Transfer the yellow solution (of sodium chromate) to two adjacent cavities of a spot plate and perform the following tests.

(i) Acidify one part with acetic acid and add a drop of lead acetate solution. A yellow precipitate of lead chromate (PbCrO_4) appears.

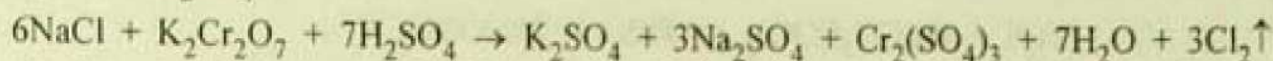
(ii) Acidify the other part with dilute sulfuric acid and add a drop of alcoholic solution of diphenylcarbazide. A violet colouration appears.

Reactions :



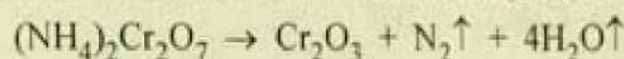
(*cf.* Sect. 4.13 and 5.18 for reactions of Chromate with diphenylcarbazide)

Some chlorine gas may also be liberated due to oxidation of chloride by $K_2Cr_2O_7$ in presence of hot conc. H_2SO_4 .



Fluorides produce volatile chromyl fluoride (CrO_2F_2), which is decomposed by water and interferes with the chromylchloride test. Bromide and iodides are oxidized to free halogens, which on reaction with NaOH solution are transformed to colourless corresponding oxyhalides, and do not interfere. If much iodide is present, iodine formed in the reaction may be oxidized to iodic acid by chromic acid formed *in situ*. In presence conc. H_2SO_4 , especially under hot condition, iodic acid may oxidize chlorides to liberate chlorine gas with regeneration of iodide, which again reacts and renders the chromyl chloride test a failure. Chlorides of mercury, because of their covalent nature, do not respond to chromyl chloride test. Chlorides of Pb, Ag, Sb, Sn etc. react only partially.

CAUTION : Ammonium dichromate should not be used in this test in place of potassium dichromate, since ammonium dichromate on heating explodes violently :

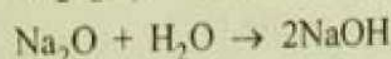
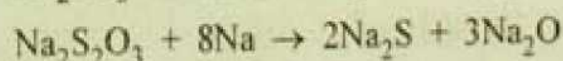
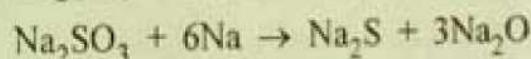
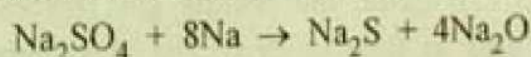


Note : For detecting chromate/dichromate, perform the same test taking a chloride salt, such as KCl, NaCl, in place of $K_2Cr_2O_7$ and proceed as usual.

6.13. Reductive Fusion Test with Metallic Sodium (or Potassium)

Test for sulfur acids

Take a small quantity (<0.1g) of the solid sample in a dry fusion tube, warm gently to remove water of crystallization if any. To the anhydrous residue of the sample add a small piece of metallic sodium (or potassium). Heat the fusion tube gently at first and then to dull redness until fusion occurs. Continue heating for 2-3 minutes. Cool to room temperature and crush the fused mass in a mortar-pastle containing little water. Triturate and filter (Figs. 3.19-3.21). The alkaline filtrate contains sodium sulfide if sulfur acids are present in the sample, as molten metallic sodium reduces these to sulfide. Thiocyanate remains unchanged. Oxyhalides are reduced to halide. Nitrate and nitric acid are reduced to ammonia which volatilizes.



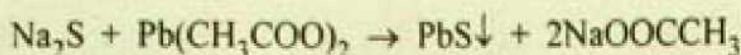
CAUTION : Do not use excess of metallic sodium (or potassium), to avoid explosion and fire due to the formation of H_2 gas during extraction of the fused mass with water.



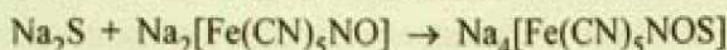
Perform the following tests with the filtrate. Positive tests indicate the presence of sulfur acids ; viz, sulfate/sulfite/thiosulfate/sulfide thiocyanate.

(i) Place a drop of the filtrate on a spot plate, add drops of dilute acetic acid until acidic

and then add a drop of lead acetate solution. Black precipitate of lead sulfide indicates sulfur acids.

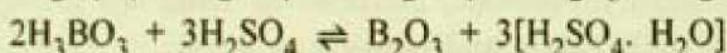
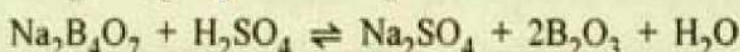
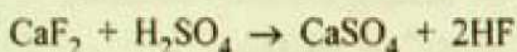


(ii) To a drop of the filtrate on a spot plate add one drop of freshly prepared sodium nitroprusside solution. A transient purple colouration indicates sulfur acids.



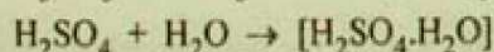
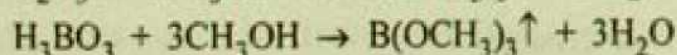
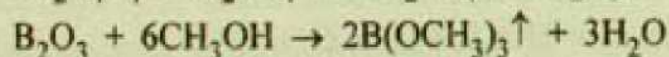
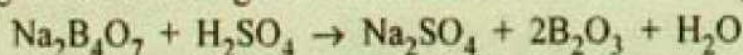
6.14. Tests for Borate and Free Boric Acid

(a) **Boron trifluoride test** : Mix a small quantity (< 0.1g) of the sample with four times its bulk of calcium fluoride on a watch glass. Add 2-3 drops of concentrated sulfuric acid and stir with a glass rod to make paste. Hold some of this paste on a platinum wire loop just out side the base of the non-luminous flame of the Bunsen burner with out touching it. A green colouration of the flame due to boron trifluoride is observed if borate or free boric acid is present.

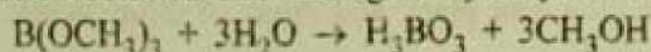


Note : Although copper and barium compounds produce green colouration to Bunsen flame, but they do not interfere with the borate test if conducted by the procedure described above. Due to greater volatility of boron trifluoride, it imparts green colouration to the flame even the borate-fluoride- H_2SO_4 paste is held out side the flame without touching it. But copper and barium flames appear only when their halide salts are held touching the Bunsen flame, since these are non-volatile.

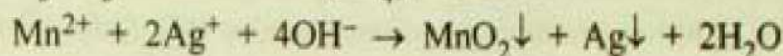
(b) **Methyl borate test** : Place a small quantity (< 0.1g) of the solid sample in a semi-micro test tube, add 1-2 ml of methanol, followed by a few drops of concentrated sulfuric acid. Fix a bent glass tube fitted with a rubber cork at the mouth of the test tube (Fig. 3.30a). Place the test tube on a hot water bath (Fig. 3.15). Ignite the issuing gas [trimethyl borate ester, $\text{B}(\text{OCH}_3)_3$]. The gas burns with green flame at the mouth of the glass tube.



(c) **Spot test** : Perform the methyl borate test as described above by holding a drop of an aqueous solution of a mixture of potassium fluoride, manganous nitrate and silver nitrate in a capillary glass dropper at the mouth of the reaction tube (Fig. 3.29b). A black precipitate is formed in the glass tube. The methyl borate gas, produced in the reaction, is absorbed in the potassium fluoride solution and undergoes hydrolysis to produce boric acid.



Boric acid reacts with potassium fluoride, producing potassium fluoroborate, $K[BF_4]$ and KOH . In presence of caustic alkali (KOH), silver nitrate oxidizes manganous nitrate to black MnO_2 and itself is reduced to black metallic silver



If a small amount of benzidine solution in acetic acid is added to the reagent (i.e. mixture of $Mn(NO_3)_2$, $AgNO_3$ and KF), MnO_2 formed in the reaction oxidizes colourless benzidine to benzidine blue (cf. Sects. 4.16, 5.14).

(d) **Tests for free boric acid** : Both borate salts and free boric acid (H_3BO_3) are indicated by the tests (a) (b) and (c) conducted with conc. H_2SO_4 , which transforms borates into boric acid or boric anhydride (B_2O_3). If these tests are positive, either H_3BO_3 or borate or both may be present. To be sure as to whether free boric acid alone is present, not the borate salts, the methyl borate test should be carried out without using conc. H_2SO_4 . If this test is positive, then free boric acid (H_3BO_3) is present, not any borate salt.

6.15. Catalysis of Iodine-Azide Reaction

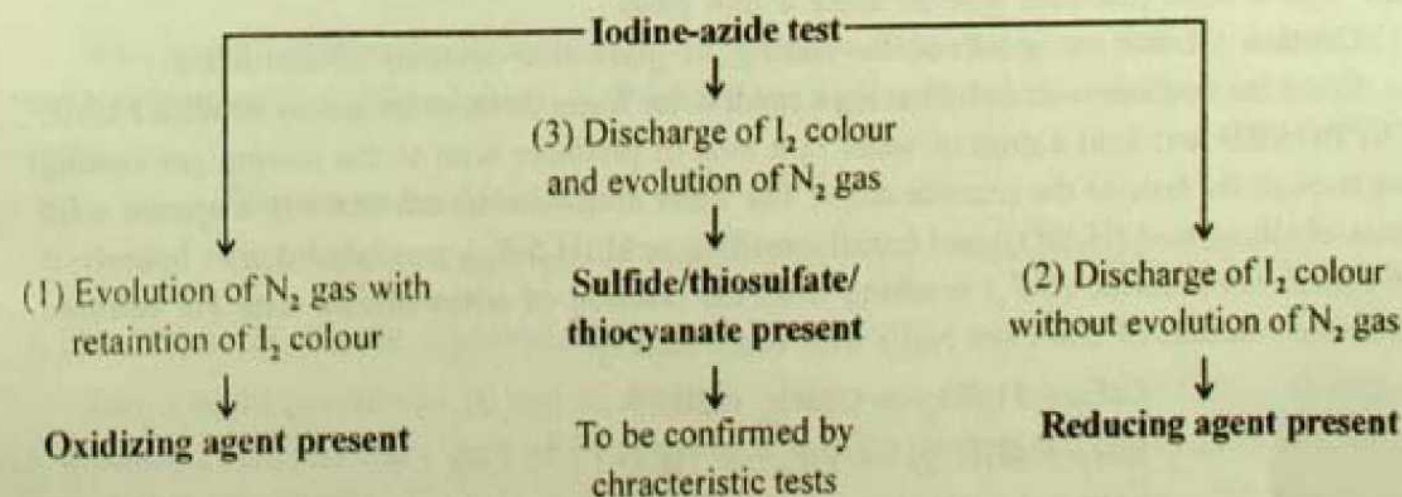
Test for sulfide, thiosulfate, thiocyanate

Reduction of iodine solution by sodium azide normally takes place very slowly, involving very slow discharge of iodine colour with evolution of N_2 gas.



But the reaction takes place very rapidly in the presence of sulfide, thiosulfate and thiocyanate. In presence of other reducing agents, only the iodine colour is discharged without evolution of gas (N_2). Whereas, in presence of oxidizing agents, such as permanganate, dichromate, iodate, bromate, Fe^{3+} ion etc. iodine colour is retained but azide is oxidized to nitrogen gas. Observations (1-3) and the corresponding inferences of iodine-azide test are summarized below:

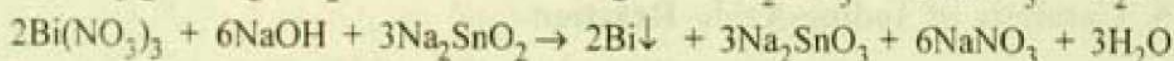
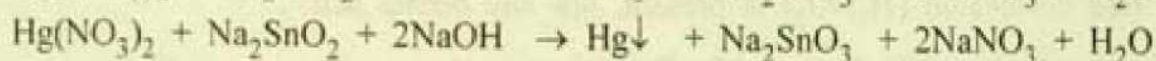
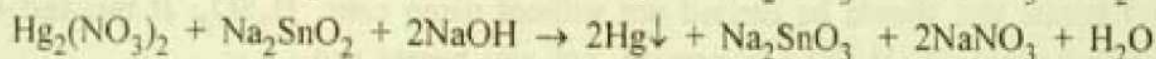
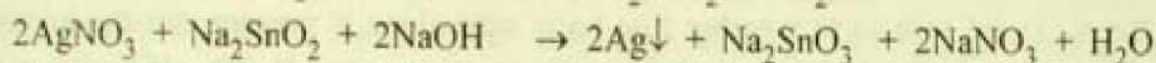
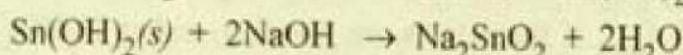
Take 2 drops of iodine-azide reagent on a spot plate, add a pinch of the solid sample and stir with a glass rod and observe the changes.



6.16. Action of Sodium Stannite Solution

Test for Ag, Hg and Bi salts

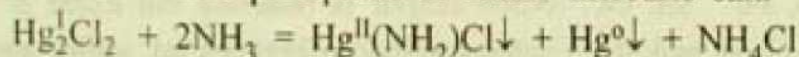
Take 1-2 drops of stannous chloride solution in a semi-micro centrifuge tube, add drops of sodium hydroxide ($\sim 2M$) solution, until the white precipitate of Sn(OH)_2 that is initially formed, passes into alkali solution producing sodium stannite (Na_2SnO_2). Place the test tube on a hot water bath (Fig. 3.15) for 2-3 minutes, centrifuge and transfer a drop of the clear centrifugate to a cavity of the spot plate containing small amount ($\sim 10 \text{ mg}$) of the sample. Immediate blackening due to reduction of the metal ions to finely divided metals indicates the presence of Ag, Hg and Bi-salts.



Note : The test may be applied on the solid sample if it is not originally black coloured, otherwise the test may be applied on a drop of the solution of the sample.

6.17. Action of Ammonia Solution [Test for Hg(I)]

To a small amount ($< 10 \text{ mg}$) of the sample on a spot plate add one drop of ammonia solution. Immediate blackening indicates Hg(I) salt. In presence of ammonia solution, which is alkaline in nature, Hg(I) undergoes disproportionation (*cf.* Sect. 2.4 (j, l)) to black metallic mercury and infusible white precipitate of amino mercuric salt.

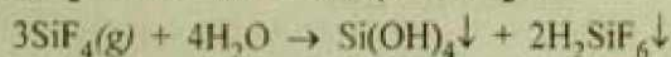
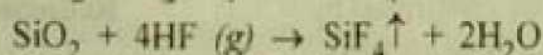


6.18. Silicon Tetrafluoride Test for Silica or Silicates/Silicic acid.

Mix a small quantity ($< 0.1 \text{ g}$) of the solid sample with one third of its weight of calcium fluoride or sodium fluoride in a lead or platinum crucible. Add drops of conc. H_2SO_4 and stir with a stout platinum wire to make a thin paste.

Caution : Don't use glass rod for mixing, as glass also contains silica/silicate.

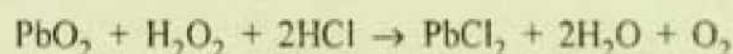
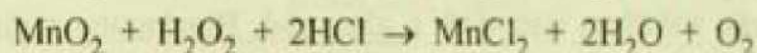
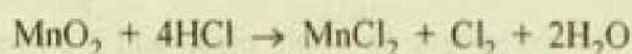
Cover the crucible with its lid having a small hole. Warm the mixture gently inside a **FUME CUPBOARD** and hold a drop of water in a loop of platinum wire to the issuing gas coming out through the hole of the crucible cover. The water drop soon transforms into a opaque solid mass of silicic acid (H_2SiO_4) and hexafluorosilicic acid (H_2SiF_6), produced due to hydrolysis of silicon tetrafluoride (SiF_4) resulting from the reaction of silica/silicate with HF released from the reaction of CaF_2 (or NaF) with conc. H_2SO_4 .



Now place the opaque mass containing Si(OH)_4 and H_2SiF_6 on a spot plate, add a drop of conc. HNO_3 , one drop of ammonium molybdate reagent and a crystal of sodium or ammonium acetate and finally add a drop of benzidine reagent in acetic acid (*cf.* Sect. 5.21). A blue colouration indicates silica or silicate. Run a blank test using all the reagents except the opaque mass obtained in the SiF_4 test.

6.19. Action of ($\text{H}_2\text{O}_2 + \text{HCl}$) Solution

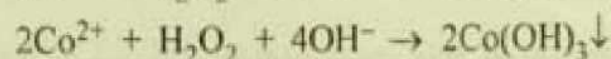
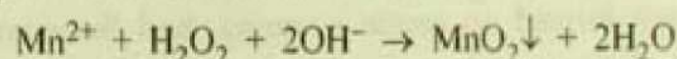
Oxidizing agents such as MnO_2 , PbO_2 , Pb_3O_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, etc. are reduced by H_2O_2 in acid medium. This is indicated by disappearance of colours of these materials. Similarly, sulfide thiosulfate, iodide etc. are oxidized by H_2O_2 . Sulfides of transition metals and post-transition metals are coloured. Oxidation of sulfide is indicated by bleaching of the colours of these sulfides.



Take a small amount ($\sim 10 \text{ mg}$) of the black coloured solid sample on a spot plate, add 1 drop of (1:1) HCl , 1-2 drops of 6% H_2O_2 (20-volume) and stir with a glass rod. Bleaching indicates any of the above type of reactions.

6.20. Action of ($\text{H}_2\text{O}_2 + \text{NaOH}$) Solution

Compounds of transition metals, eg, Mn, Fe, Co, Ni, Cu undergo blackening due to oxidation of the metal ions and precipitation of oxides or hydroxides in their higher oxidation states. Sulfide (S^{2-}), if present, is oxidized to sulfate :



Take a small amount ($\sim 10 \text{ mg}$) of the solid sample on a spot plate, add 1-2 drop of 6% H_2O_2 (20-volume), 1 drop of dilute ($\sim 2 \text{ M}$) sodium hydroxide solution and stir with a glass rod :

Blackening $\rightarrow \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} etc.

Bleaching $\rightarrow$ Oxidation of black sulfides (e.g. PbS) to sulfate (PbSO_4).

6.21. Action of Ferric Chloride Solution

Take a small quantity ($\sim 10 \text{ mg}$) of the solid sample on a spot plate, add 1 drop of dilute hydrochloric acid and add 1 drop of ferric chloride solution. Stir with a glass rod and observe any change of colour.

- (i) Blood red colouration $\rightarrow$ Thiocyanate.
- (ii) Prussian blue colouration $\rightarrow$ Ferrocyanide.
- (iii) Brown colouration, turns blue on addition of starch $\rightarrow$ Iodide.

6.22. Action of Ferrous Sulfate Solution

Take a small amount (~ 10 mg) of the solid sample on a spot plate, add 1 drop of dilute sulfuric acid and a crystal of ferrous sulfate or Mohr's salt. Stir with a glass rod and observe any change of colour.

- (i) Bleaching $\rightarrow$ Presence of oxidizing agent, eg, MnO_2 , $\text{Cr}_2\text{O}_7^{2-}$.
- (ii) Dark blue colouration $\rightarrow$ Ferricyanide.

6.23. Action of Ammoniacal Silver Nitrate Solution

To a small quantity (~ 10 mg) of solid sample on a spot plate, add 1-2 drops of *aq*-ammonia and 1 drop of silver nitrate solution, stir with a glass rod. Blackening indicates Mn, Fe, Co, Ni, Cr (green), due to precipitation of higher valent oxides of the transition metals and black metallic silver.

6.24. Tests for Phosphate, Arsenate (also Arsenite)

Take a small quantity (~ 10 mg) of the sample in a semi-micro test tube, add ~ 0.5 ml of concentrated nitric acid and heat gently for 2-3 minutes. Cool and dilute with 1-2 ml of water, allow to settle or centrifuge if necessary. Perform the following tests with the clear supernatant liquid.

- (a) To 1-2 drops of the HNO_3 extract, add ~ 10 -15 drops of ammonium molybdate reagent and heat gently on a hot water bath (Fig. 3.15).

A canary yellow precipitate indicates phosphate.

If a yellow precipitate is not formed on gentle warming, boil the mixture gently for 2-3 minutes.

A canary yellow precipitate at this stage indicates arsenate also arsenite, since arsenite is oxidized to arsenate by hot concentrated nitric acid.

- (b) If a canary yellow precipitate appears in the above test (a), take in another test tube, 1-2 drops of the HNO_3 extract, add a few crystals of tartaric acid and ~ 10 -15 drops of ammonium molybdate reagent. Boil the mixture gently for 2-3 minutes. Two cases may arise :

- (i) *A canary yellow precipitate is formed.*

A canary yellow precipitate in this test indicates the presence of phosphate, but does not indicate the absence of arsenate.

- (ii) *Canary yellow precipitate is not formed*

A canary yellow precipitate in test (a) and no such precipitate in this test indicates the presence of arsenate.

These observations and inferences may be summarized as follows :

	Reagent(s)/Conditions	Observations	Inferences
(a)	(i) $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$, warming	Canary yellow precipitate	PO_4^{3-}
	(ii) $(\text{NH}_4)_2\text{MoO}_4 + \text{HNO}_3$, boiling. If test (a) is positive, perform test (b).	Canary yellow precipitate	AsO_4^{3-} (also PO_4^{3-})
(b)	$(\text{NH}_4)_2\text{MoO}_4 + \text{tartaric acid} + \text{HNO}_3$, boiling	Canary yellow pricipitate	PO_4^{3-}
		No precipitate	AsO_4^{3-}

Note : Arsenite, if present, is oxidized to arsenate by HNO_3 in hot condition and responds to this test.



CHAPTER - 7

Systematic Wet Tests for Cation and Anion Radicals

7.1 Introduction

Preliminary tests described earlier (Ch. 6) give indications or, clues to the presence or absence of most of the radicals except a few, viz, Pb, Cd, Bi, Al, Mg for which there are no suitable preliminary tests. Wet tests are first carried out for those radicals for which indications have been obtained from the preliminary tests, and these radicals are to subsequently confirmed by unambiguous confirmatory tests.

7.2 Preparation of Test Solutions

(a) Aqueous or acid extract for detection of cations

Before carrying out the wet tests, it is essential to bring the sample, or, part thereof into solution. For examination of metal ions (cations), solubility of the sample has to be tested in the following solvents, exactly in the order as given below, first in the cold condition and then on warming and on boiling conditions.

- (1) water,
- (2) dilute hydrochloric acid,
- (3) concentrated hydrochloric acid,
- (4) dilute nitric acid,
- (5) concentrated nitric acid,
- (6) aqua-regia.

To ensure whether the sample or part thereof has dissolved in a particular solvent, place 1-2 drops of the extract of the sample on a watch glass and evaporate to dryness on a hot water bath. If a residue is left on the watch glass, it may be taken as granted that the sample or a part thereof has dissolved in that particular solvent.

If the sample or a part thereof is soluble in water, proceed to test for cations in this solution.

If on addition of dilute hydrochloric acid to the sample a precipitate is formed, which may be due to the chlorides of Ag(I), Hg(I) and Pb(II) of Group-I, then try to dissolve the original sample in dilute HNO_3 . If concentrated hydrochloric acid is used to dissolve the sample, then the resulting solution should be evaporated inside a **FUME CUPBOARD** to remove most of the acid, otherwise in presence of high concentration of acid, copper and arsenic group metal sulfides (Group IIA and IIB) will not be completely precipitated. If the solution is made in nitric acid (dilute or concentrated) or in aqua-regia, the solution to be evaporated to dryness inside a **FUME CUPBOARD**, followed by evaporation with little hydrochloric acid to a small volume and finally diluting with water. Otherwise, oxidizing action of nitric acid and aqua-regia may obscure the tests for cations, particularly of Group -II analysis.

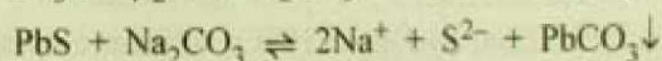
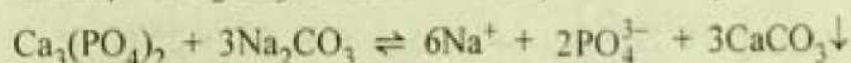
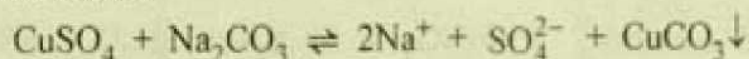
After a suitable solvent is found, the main bulk of the solution for cation analysis has to be prepared. For this purpose, take ~0.1-0.5 g of the solid sample in a small 25-50 ml conical flask add 10-15 ml of the selected solvent, boil the mixture gently for ~10 minutes covering the mouth of the conical flask with a small funnel (Fig. 3.12). Add small amount of the solvent if necessary to compensate for the loss on evaporation. Filter under hot condition (Fig. 3.21), wash with small amount of the solvent, cool the solution to room temperature. Treat the residue, if any, with the next solvent in the order recommended above. If a permanent residue is left, even after treatment with aqua-regia, the residue should be treated as an "*insoluble part*" for which there are special treatments.

(b) NaOH extract: (for detection of ampholytes)

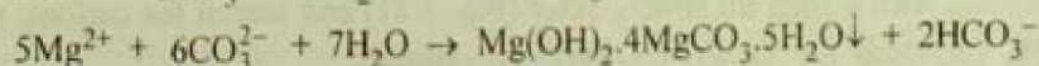
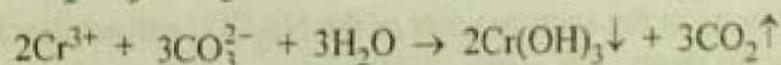
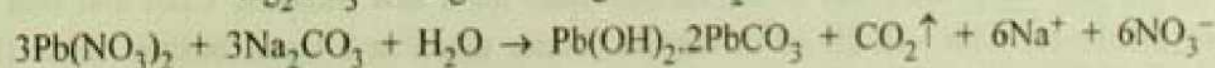
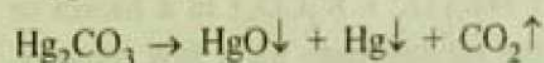
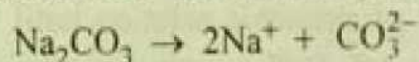
Digest ~0.2g of the solid sample with sodium hydroxide solution (10%) by gentle boiling, centrifuge, and discard the residue. The extract may contain the amphoteric radicals, eg, PbO_2^{2-} , AlO_2^- , ZnO_2^{2-} , AsO_4^{3-} , AsO_2^- , $\text{SnO}_2^{2-}/\text{SnO}_4^{4-}$, BO_3^{3-} , SiO_3^{2-} which may be tested individually [also, MoO_4^{2-} , WO_4^{2-} , VO_3^-]*

(c) Sodium carbonate extract: (for detection of anions)

Solution for testing the anions, should be free from heavy metals or metals other than alkali metals. Such a solution is best prepared by boiling the sample with a concentrated solution of sodium carbonate. Double decomposition reactions take place between sodium carbonate and the metallic salts present in the sample. Since the carbonates of most metals other than the alkali metals are sparingly soluble, these are precipitated, and the anions of the salts remain in solution as sodium salts:

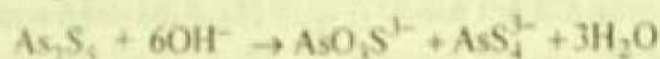
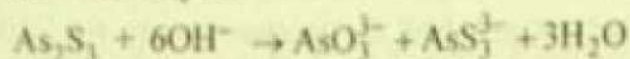


Certain metallic carbonates, after initial formation, are converted into basic carbonates or eventually into hydroxides, due to the basic nature of sodium carbonate (*cf.* Sect 2.1)



*Rare elements

Due to alkaline nature of sodium carbonate solution, sulfides of As, Sb, Sn are transformed to soluble oxy-, thio- and oxythio- salts.

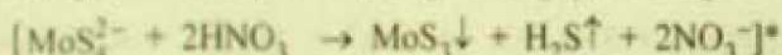
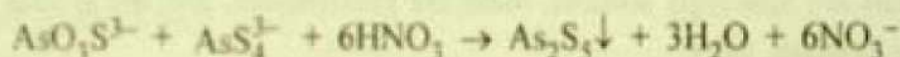


Similar reactions occur with antimony and tin sulfides.

Procedure

Take ~0.2-0.5g of the sample in a small conical flask (~50 ml) add 15-20 ml of a saturated solution of sodium carbonate (~1.5M or 4g anhydrous Na_2CO_3 and 25 ml of distilled water). Cover the flask with a small funnel (Fig 3.12) and boil the mixture gently for ~10 minutes. Filter (Fig. 3.21) wash the residue with distilled water. Collect the combined filtrate and the washings (Na_2CO_3 - extract) for detection of anion radicals. Treat the residue of the Na_2CO_3 extract with dilute hydrochloric acid. The undissolved portion if any maybe treated as an *insoluble material*.

Add dil. HNO_3 to the Na_2CO_3 extract, but not sufficient to neutralize the solution. At this stage basic copper salt or copper oxide may precipitate out if the Na_2CO_3 extract has a bluish colour due to the presence of complex copper (II) carbonate. Filter off the precipitate and acidify the filtrate with dilute HNO_3 , boil for 1-2 minutes to remove CO_2 gas completely. If any precipitate is formed at this stage, add more dil. HNO_3 to ensure complete precipitation of the substance. Mainly the thio- and oxythio- salts of As, Sb Sn (also V, Mo, W)* decompose on acidification with precipitation of the corresponding sulfides:



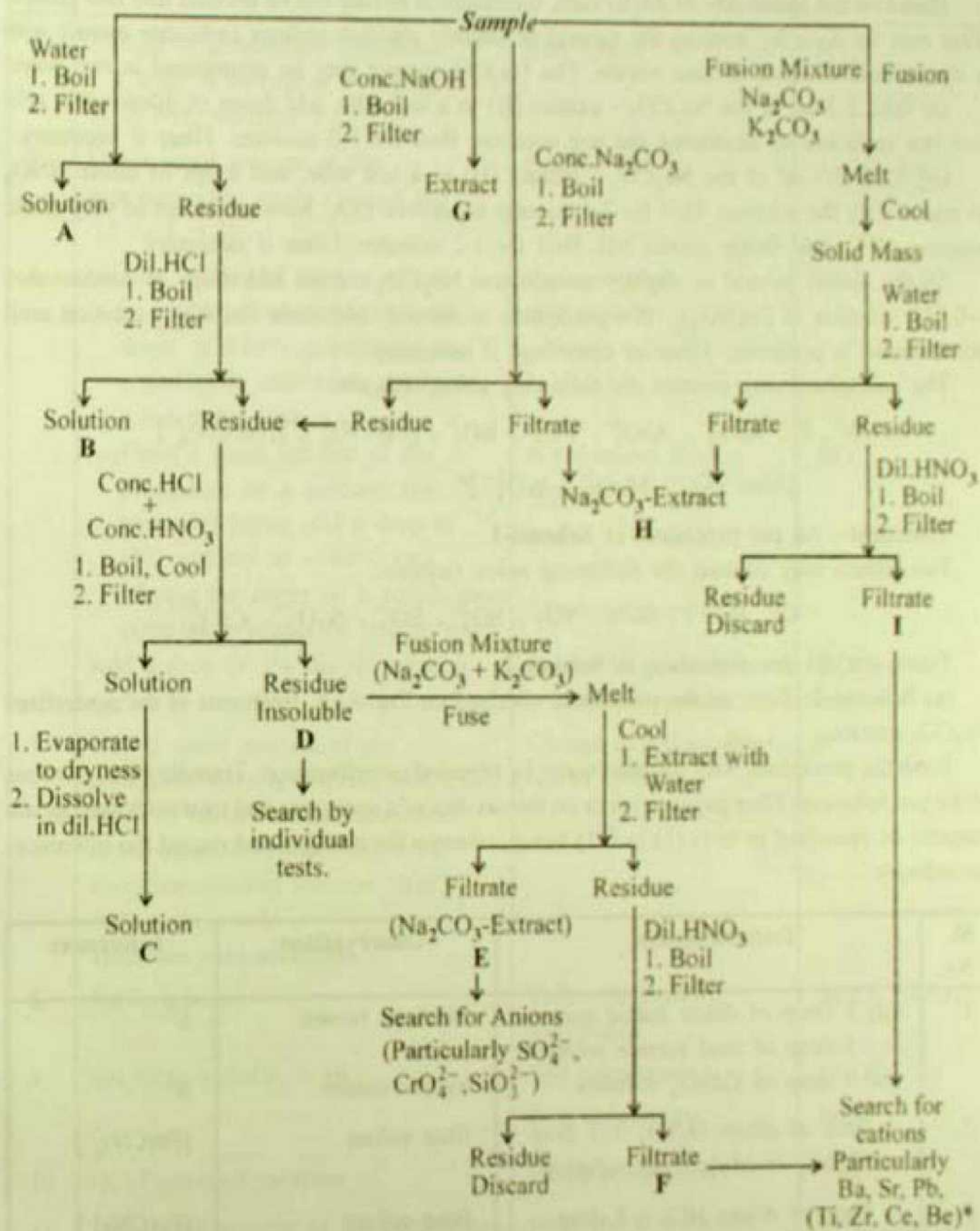
If a precipitate appears on acidification, add more HNO_3 to ensure complete precipitation. Filter and search for As, Sb, Sn, (V, Mo, W)* in the precipitate. Boil the filtrate to remove H_2S completely.

To the acidified Na_2CO_3 extract, add drops of ammonia solution until faintly ammoniacal. If any precipitate appears at this stage filter it off. Boil to remove excess ammonia if any. The Na_2CO_3 -extract is now almost neutral and is ready for testing for the anion radicals.

If the original substance is an insoluble material, mix ~0.2-0.5 g of the substance with 4 times its bulk of fusion mixture (1:1 $\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3$) in a nickel or a platinum spoon. Heat to fusion and keep the mass in the molten state for a few minutes. Cool and boil the mass for ~5 minutes with ~15-20 ml of distilled water taken in a small beaker. Filter (Fig. 3.21) and process the filtrate in the same manner as the Na_2CO_3 extract described above. Digest the residue with a little dil. HNO_3 , filter (Fig. 3.21) and search for cations, particularly for Ba, Sr, Pb, Ca, (also for Ti, Zr, Ce, Be)* accordingly.

*Rare elements

The methods of preparation of solution of the sample are summarized below:



*Rare elements

7.3 Scheme for Detection of Anion Radicals in Na_2CO_3 -Extract H

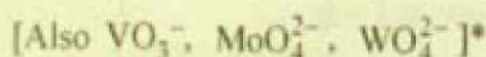
Based on the solubility of Zn(II) salts, the common anions can be divided into two groups. This may be done by treating the neutral or slightly alkaline sodium carbonate extract with a concentrated solution of zinc nitrate. The Na_2CO_3 -extract may be neutralized in two ways:

(i) Take 2-3 ml of the Na_2CO_3 - extract (H) in a test tube, add drops of dilute nitric acid just not sufficient to neutralize the test solution. Boil for 1-2 minutes. Filter if necessary.

(ii) Take 2-3 ml of the Na_2CO_3 - extract (H) in a test tube, add drops of dilute HNO_3 to just acidify the solution. Boil for 2-3 minutes to remove CO_2 . Now add drops of very dilute aqueous NH_3 until faintly smells NH_3 . Boil for 1-2 minutes. Filter if necessary.

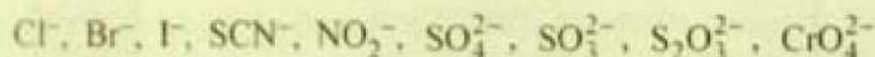
To the almost neutral or slightly ammoniacal Na_2CO_3 extract add drops of concentrated ($\sim 0.5M$) solution of $\text{Zn(NO}_3)_2$. If a precipitate is formed, add more $\text{Zn(NO}_3)_2$ solution until precipitation is complete. Filter or centrifuge if necessary.

The precipitate may contain the following anion radicals:



Treatment : As per procedure in **Scheme-1**.

The filtrate may contain the following anion radicals:



Treatment: As per procedure in **Scheme-2**.

(a) **Scheme-1**: Tests on the precipitate obtained on $\text{Zn(NO}_3)_2$ treatment of the neutralized Na_2CO_3 -extract.

Wash the precipitate with distilled water by repeated centrifugation. Transfer small portions of the precipitate on filter paper strips or on the cavities of a spot plate and treat with appropriate reagents as described in tests (1) to (11) below, observe the changes and record the inferences accordingly.

Sl. No.	Tests/Reagents	Observations	Inferences
1.	(a) 1 Drop of dilute acetic acid + 1 drop of lead acetate solution (b) 1 drop of CdSO_4 solution	Black or brown colour Yellow colour	S^{2-} S^{2-}
2.	1 Drop of dilute H_2SO_4 + 1 drop of FeSO_4 or Mohr's salt solution	Blue colour	$[\text{Fe(CN)}_6]^{3-}$
3.	1 Drop of dilute HCl + 1 drop FeCl_3 solution	Blue colour	$[\text{Fe(CN)}_6]^{4-}$

*Rare elements

Sl. No.	Tests/Reagents	Observations	Inferences
4.	1 Drop of ammonium molybdate + 1 drop of benzidine + 1 drop of aq-NH_3 solution.	Blue colour	PO_4^{3-}
5.	Dry a small amount of the precipitate and apply Gutzeit test (cf. Sect. 4.8)	Positive test	AsO_4^{3-} , AsO_3^{3-}
6.	(i) Take a little of the precipitate in a semi-micro test tube, add 3 drops of 0.01% quinalizarin in conc. H_2SO_4 and warm gently on a hot water bath. (ii) Place a small amount of the precipitate on a curcuma (or turmeric) paper, add a drop of HCl and dry at $\sim 100^\circ\text{C}$ by, placing the paper on a watch glass covering a beaker of boiling water. Add a drop of 1% NaOH solution.	Violet to blue colouration A red-brown fleck appears. A blue to greenish black colouration appears	BO_3^{3-} , B_2O_3 BO_3^{3-} BO_3^{3-}
7.	Take a small amount of the precipitate on a spot plate, add 1-2 drops of barium chloride solution and a drop of hydrochloric acid-zirconium-alizarin solution. Stir with a glass rod. Tests for rare elements	Change of colour from red to yellow	F^-
8.	SnCl_2 solution	Yellow to brown colouration	MoO_4^{2-} , WO_4^{2-}
9.	$\text{NH}_4\text{SCN} + \text{SnCl}_2 + \text{HCl}$	Red colouration Blue colouration	MoO_4^{2-} , WO_4^{2-}
10.	HCl -Potassium xanthate	Violet colouration	MoO_4^{2-}
11.	To a small amount of the precipitate on a spot plate, add 1 drop of dilute H_2SO_4 and 1-2 drops of 6% H_2O_2 solution.	Wine red colouration	VO_3^-

(b) Scheme-2 : Tests on the filtrate after $\text{Zn}(\text{NO}_3)_2$ treatment of Na_2CO_3 extract.
 Perform the following tests on spot plate, filter paper or in test tubes as required.

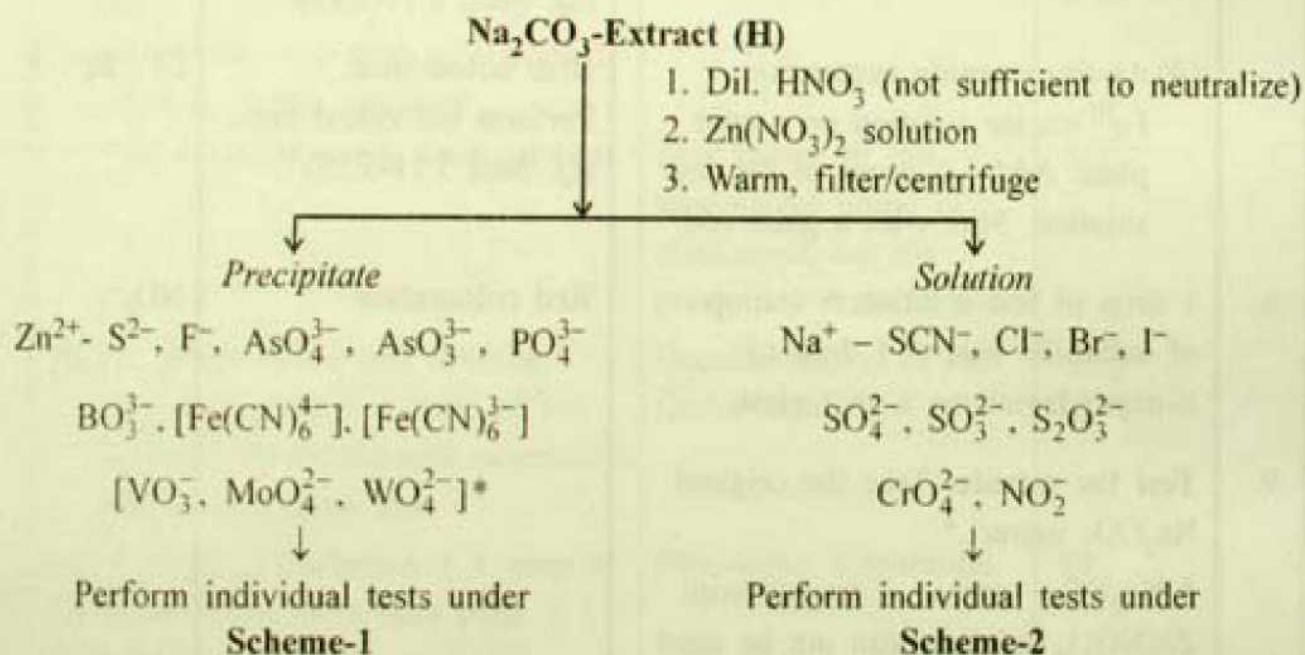
Sl. No.	Tests/Reagents	Observations	Inferences
1.	1 drop of test solution + 1 drop of HCl + 1 drop of FeCl_3 solution	Intense red colouration	SCN^-
2.	(i) 1 drop of test solution + 1 drop of $\text{dil.H}_2\text{SO}_4$ + 1 drop of diphenyl carbazide	Violet colouration	CrO_4^{2-}
	(ii) 1-2 drops of test solution + 3-4 drops of $\text{dil.H}_2\text{SO}_4$ + 1-2 drops of 6% H_2O_2 + 1 ml of ether, shake.	Blue etherial layer	CrO_4^{2-}
3.	(i) 1-2 drops of test solution + 3-4 drops of dil.HNO_3 + 1 drop of dil.KMnO_4 + 1 drop of $\text{Ba}(\text{NO}_3)_2$ solution, shake, centrifuge. Add drops of oxalic acid solution.	Pink coloured precipitate Pink colour of the supernatant liquid is discharged, but the precipitate remains pink	SO_4^{2-} SO_4^{2-}
	(ii) 1-2 drops of the test solution on a spot plate + 1 drop of red coloured Ba-rhodizonate suspension. Stir with a glass rod.	Decolourization of red flecks occur	SO_4^{2-}
4.	1-2 drop of test solution + 1 drop of fuchsin-bisulfite on a spot plate + 1 drop of Cl_2 -water.	Blue-violet colouration	Br^-
5.	1 drop of blue coloured I_2 -KI-starch solution on a spot plate + drops of the test solution. Test the decolourised solution with litmus papers	Discharge of blue colour Blue remains blue, red remains red. <i>Neutral.</i> Blue changes to red. <i>Acidic.</i>	Reducing agents* S^{2-} , $\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} S^{2-} , $\text{S}_2\text{O}_3^{2-}$ SO_3^{2-}

*Note: If these sulfur acids are present, remove them from the solution before testing for halides with AgNO_3 solution (cf. test-7).

Sl. No.	Tests/Reagents	Observations	Inferences
6.	Take 1-2 ml of the test solution in a semi-micro test tube, warm slightly, add a pinch of PbCO_3 .	Brown to black colouration	$\text{S}_2\text{O}_3^{2-}$, S^{2-}
7.	Filter/Centrifuge the resulting solution after test (6), discard the precipitate. To the clear centrifugate, add drops of $\text{Sr}(\text{NO}_3)_2$ solution and filter/centrifuge off any precipitate that may appear at this stage. Perform the following tests with the clear solution.		
8.	(i) 1-2 drops of test solution + 1-2 drops of dil.HNO_3 + 1 drop of AgNO_3 solution.	Curdy white to pale yellow to yellow precipitate. Perform individual tests. (cf. Sect. 5.11-5.15)	Cl^- , Br^- , I^-
	(ii) Ag-ferrocyanide suspension + Fe^{III} -nitrate solution on a spot plate. Add 1-2 drops of the test solution. Stirr with a glass rod.	Blue colouration. Perform individual tests, (cf. Sect 5.11-5.15)	Cl^- , Br^- , I^-
	1 drop of test solution + 1 drop of sulfanilic acid + 1 drop of α -naphthylamine on a spot plate	Red colouration	NO_2^-
	Test for nitrate. Take the original Na_2CO_3 extract.* * Na_2CO_3 - extract, if treated with $\text{Zn}(\text{NO}_3)_2$ solution, can not be used for testing nitrate. To 1 drop of the test solution on a spot plate, add 1 drop of HCl , + 1 drop of sulfanilic acid + 1 drop of α -naphthylamine.	(i) No red colouration (ii) Red Colouration	NO_2^- absent NO_2^- present
	(i) If NO_2^- is absent. Add a few grains of zinc dust and stirr with a glass rod.	Red colouration	NO_3^-

Sl. No.	Tests/Reagents	Observations	Inferences
	(ii) If NO_2^- is present. Decompose nitrite it by boiling the test solution with urea or sulfamic acid and $\text{dil. H}_2\text{SO}_4$. Cool the solution and test for NO_2^- as before to ensure complete removal of NO_2^- until no red colouration appears on treatment with sulfanilic acid and α-naphthylamine. Now add a few grains of Zn-dust and stir with a glass rod.	Red colouration	NO_3^-

Systematic procedure for the treatment of Na_2CO_3 -extract (H) is summarized below:

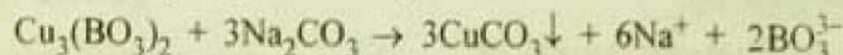
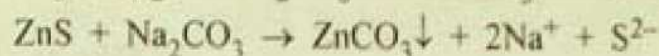
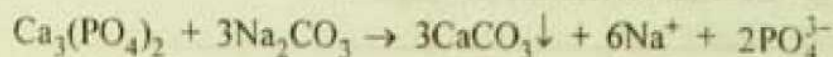


7.4 Detection of Anion Radicals in Mixtures

There is no comprehensive scheme for separation of all the anion radicals. Most of the anion radicals can be detected by their characteristic tests. Chemically similar, i.e., allied anion radicals can, however, be detected from their mixtures after 1/2/3-stage separation methods.

Since the presence of heavy metals, more specifically, metals other than alkali metals may interfere in the detection of many anion radicals, by forming precipitate or colouration, it is convenient to test for the anion radicals after removing these metals from the test solution. The easiest and most convenient way of removing the heavy metals is to precipitate them as their carbonates or hydroxides by treating the sample solution with a concentrated solution of sodium carbonate or by digesting a (1:4) mixture of the solid sample and sodium carbonate

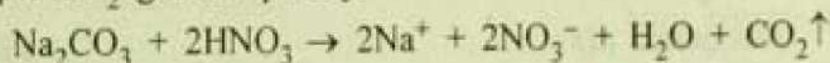
with water, when the anion radicals remain in solution in the form of their sodium salts, which may be detected by their characteristic tests with or without separation, and the heavy metals are precipitated as their carbonates or hydroxides /oxides (*cf.* Sect 7.2c)



The precipitated carbonates may be separated by filtration. The filtrate called " Na_2CO_3 -extract" contains the anion radicals as well an excess of sodium carbonate, which render the solution strongly alkaline. Carbonate radical also interferes with the tests of most of the anion radicals, since in many of such tests, the reagents are solutions of salts of metals, which form sparingly soluble carbonates and hydroxides. Therefore, before proceeding to test for anion radicals, the Na_2CO_3 extract should be neutralized with an acid and carbonte should be removed as CO_2 gas by boiling the solution. Normally the acid used for neutralization of the Na_2CO_3 extract should have the same anion as the metal salt that is subsequently added as the reagent.

Procedure for preparation of Na_2CO_3 -extract

Take ~0.2g of the powdered sample and ~4 times of its bulk of anhydrous Na_2CO_3 in a small (25–50 ml) conical flask, add just sufficient water to dissolve the Na_2CO_3 (if the sample is a liquid or a solution, add ~10g of Na_2CO_3 per ~5 ml of the solution). Cover the mouth of the conical flask with a small funnel (Fig. 3.12). Boil the mixture gently for ~15 minutes adding water to replenish the loss on evaporation. Filter (Fig 3.21) and wash with a little hot water. Discard the residue, which manly contains the carbonates and hydroxides of the heavy metals present in the sample. Acidify the combined filtrate and the washings with 8M HNO_3 . Boil gently to expel CO_2 gas completely.



Cool the solution and filter any precipitate (Note-1) that may appear at this stage. Add 2M NH_3 to the solution (or the filtrate, as the case may be) until faintly alkaline (test with litmus paper). Finally boil the filtrate gently for 2-3 minutes to expel the excess NH_3 . Filter any precipitate that may appear at this stage (Note-2). Call this filtrate as "*neutralized Na_2CO_3 extract*".

Note : (1) Sulfides of Group-IIB metals, As, Sb, Sn (also Mo, W, V)* dissolve in Na_2CO_3 solution because of its alkalinity, forming their oxy-, thio-and oxythio-salts. The corresponding sulfides are precipitated on acidification (*cf.* Sects. 4.8-4.10, 7.2c) and may be removed by filtration/centrifugation.

(2) Carbonato and hydroxo complex ions of certain metats e.g, Cu, Co, Cr, Al, Zn (also Be)* decompose on acidification of the Na_2CO_3 - extract and the metal salts remain in solution so long it is acidic. On addition of ammonia, the solution becomes alkaline and the hydroxides of the metals are precipitated which may be removed by filtration/centrifugation.

*Rare elements

(1) Mixture of sulfur acids: Sulfide, Sulfite, Thiosulfate and Sulfate

Take ~2 ml of the neutralized Na_2CO_3 -extract in a test tube, add an excess of freshly precipitated CdCO_3 , shake the mixture and filter.

Precipitate (1)

May contain CdS (yellow) and excess of CdCO_3 (white)

1. Pour drops of 2M acetic acid on the precipitate. While still on the filter paper. The excess CdCO_3 dissolves and the yellow precipitate of CdS becomes clearly visible.

Sulfide present.

2. Transfer the yellow precipitate into a test tube, add 2M HCl and warm gently. Test the issuing gas (H_2S) with filter paper spotted with:

(i) Lead acetate paper:

Black spot appears.

(ii) Alkaline sodium nitroprusside paper :

Violet spot appears.

Sulfide present.

Filtrate (1)

May contain : SO_3^{2-} , SO_4^{2-} , $\text{S}_2\text{O}_3^{2-}$

1. Add drops of 0.25M $\text{Sr}(\text{NO}_3)_2$ solution. If a white precipitate appears, add more $\text{Sr}(\text{NO}_3)_2$ until precipitation is complete. Filter and wash the precipitate with a little water.

Precipitate (2)

(white)

May contain: SrSO_3 & SrSO_4

1. Wash with little water.
2. Pour drops of 2M HCl on the precipitate while still on the filter paper and collect the effluent in a test tube.

3. Residue (3)

(white) SrSO_4

- (i) Transfer the residue into a fusion tube, evaporate to dryness, mix with 4 times its bulk of Na_2CO_3 and some active charcoal. Heat the mixture to fusion. Extract the fused mass with hot water.

4. Filtrate (3)

May contain SO_3^{2-}
(i.e., H_2SO_3)

Add a few drop of blue coloured starch-iodine solution and place the mixture on a hot water bath (Fig. 3.15). [I_2 oxidizes SO_3^{2-} to SO_4^{2-}]

Filtrate (2)

May contain SrS_2O_3 .

Divide into four parts.

Part (i): Add AgNO_3 solution.

White precipitate gradually turns yellow to brown to black.

Thiosulfate present.

Part (ii): Add dil. 2M HCl until acidic. SO_2 gas is evolved with precipitation of sulfur.

Thiosulfate present.

Part (iii): Add lead acetate solution and warm gently.

3. Residue (3)

(ii) Place 1 drop of the filtrate on a spot plate and add 1 drop of sodium nitroprusside reagent. A violet colouration indicates S^{2-} ion.

Sulfate present.

(iii) Apply $BaSO_4 - KMnO_4$ mixed crystal formation test.

(cf. p- 331, 383)

4. Filtrate (3)

Blue colour is discharged, white precipitate of $SrSO_4$ settles down.

Sulfite present.

Filtrate (2)

White precipitate appears, turns gradually black (PbS).

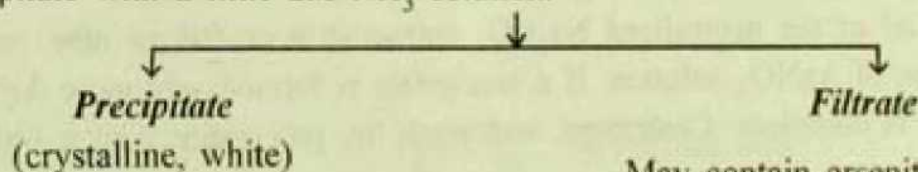
Thiosulfate present.

Part (iv): Add ammonium molybdate to the test solution and then carefully pour the mixture slowly down the side of a test tube containing 1 ml of conc. H_2SO_4 . A blue ring (*molybdenum blue*) is formed at the junction of the two liquids.

Thiosulfate present.

(2) Phosphate (PO_4^{3-}), Arsenate (AsO_4^{3-}) and Arsenite (AsO_3^{3-}) in Mixture

Take 2-3 ml of the neutralized Na_2CO_3 -extract in a small beaker, add ~2ml of 0.5 M $Mg(NO_3)_2$ or 0.5M magnesia mixture and drops of 2M NH_3 until the solution is alkaline. Warm the mixture gently on a hot water bath for ~5-10 minutes. If a white crystalline precipitate appears, add more $Mg(NO_3)_2$ or magnesia mixture solution until precipitation is complete. Filter and wash the precipitate with a little 2M NH_3 solution.



May contain: $NH_4MgPO_4 \cdot 6H_2O$ and/or
 $NH_4Mg AsO_4 \cdot 6H_2O$

1. Transfer the precipitate into a small beaker, using a small spatula (cf. Fig. 3.13b). Add 2M HCl and warm gently. The precipitate dissolves. Treat the solution with a slight excess of SO_2 -water, to reduce AsO_4^{3-} to AsO_3^{3-} . Boil off SO_2 completely.
2. Add H_2S -water. If a yellow precipitate due to As_2S_3 appears, **Arsenate (AsO_4^{3-}) is present.**
3. Add more H_2S -water to completely precipitate As_2S_3 . Filter and boil off H_2S from the filtrate, concentrate it to small a volume (~0.5 ml). Add an equal volume of conc. HNO_3 , and a few ml. of ammonium molybdate reagent. Place the mixture on a hot water bath for 2-3 minutes. If a canary yellow precipitate appears, **Phosphate (PO_4^{3-}) is present.**

May contain arsenite (AsO_3^{3-})

1. Acidity with dil. 2M HCl and add drops of H_2S -water. Yellow precipitate of arsenic sulfide appears.

Arsenite (AsO_3^{3-}) present.

(3) Nitrate (NO_3^-) and Nitrite (NO_2^-) in Mixture

Nitrate can not be detected in presence of nitrite, but nitrite can be detected in presence of nitrate.

(1) Place a drop of the neutralized Na_2CO_3 extract on a spot plate, add 1 drop of sulfanilic acid and 1 drop of α -naphthylamine in acetic acid. A red colouration indicates **nitrite**.

If a red colouration is not produced in the above test, nitrite is absent. Now add a very small amount of zinc-dust and stir with a glass rod. A red colouration at this stage indicates **nitrate**.

Sulfanilic acid is diazotized by nitrite. The red colour is produced as diazotized sulfanilic acid is coupled with α -naphthylamine. (cf. Sect 5.8). Nitrate does not react with these reagents. Zn-dust reduces nitrate to nitrite, which subsequently undergoes diazo-coupling reaction with sulfanilic acid and α -naphthylamine.

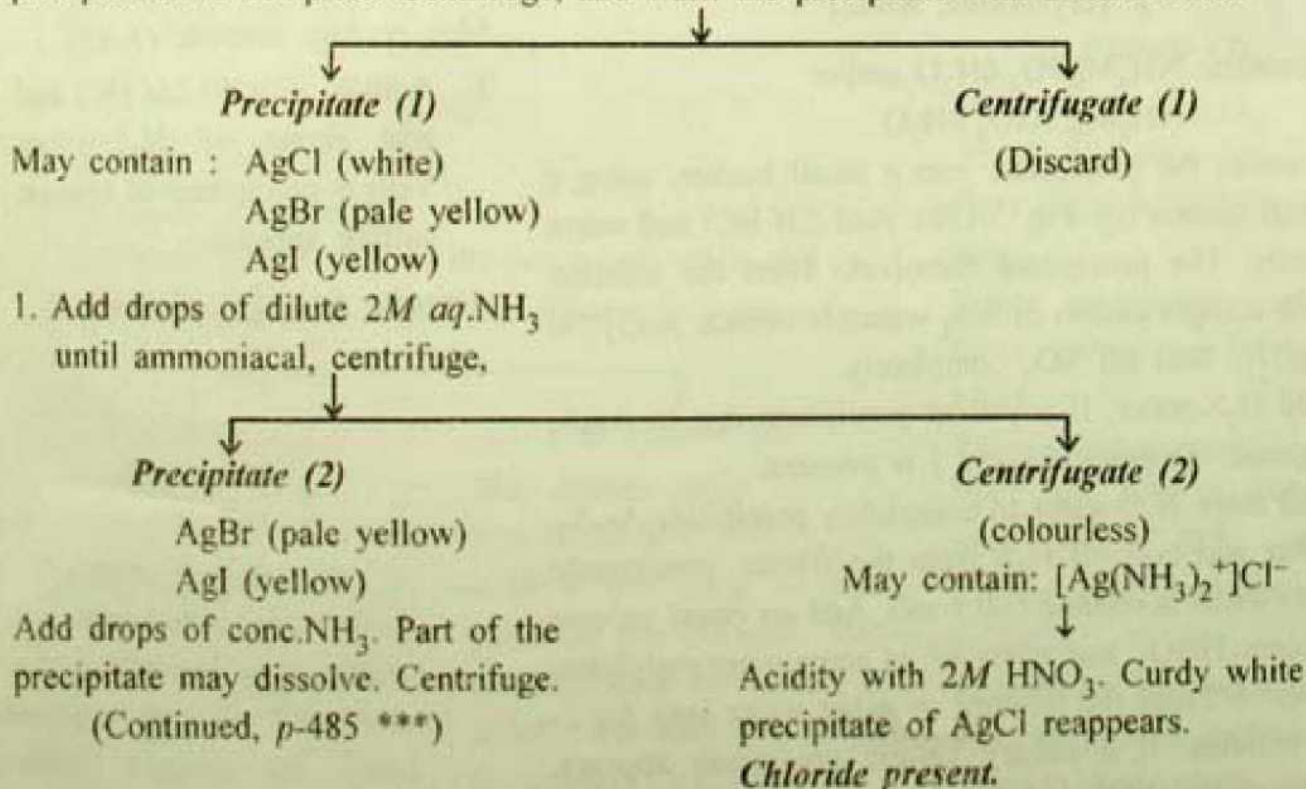
(2) If nitrite is present, it should be decomposed before proceeding to testing for nitrate. Nitrite may be decomposed by boiling the test solution with either urea, or, sulfamic acid or ammonium chloride (cf-Sect 5.3).

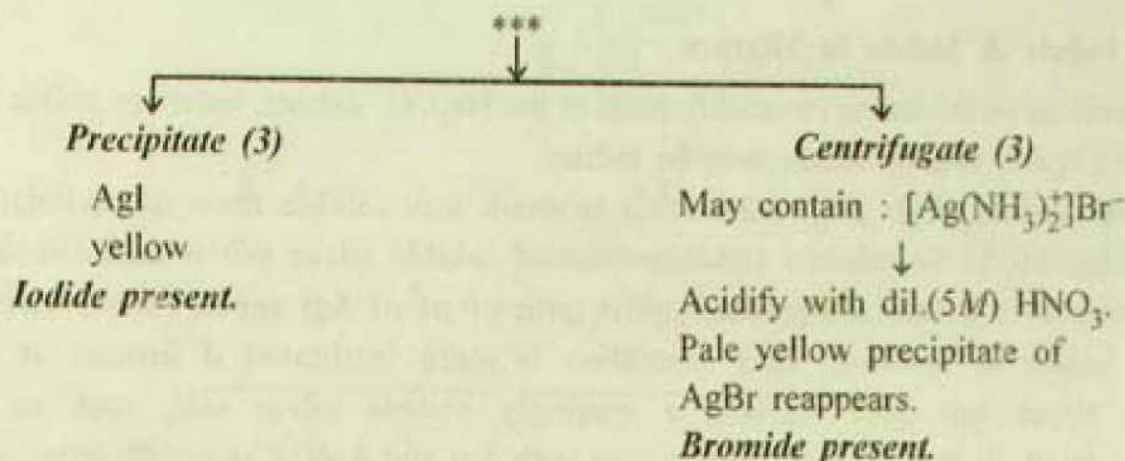
Take ~2-3 ml of the neutralized Na_2CO_3 extract in a test tube, add a few crystals of urea/sulfamic acid/ NH_4Cl , boil gently until effervescence (N_2 gas) ceases. Test for nitrite as before. If nitrite is still present, decompose it by repeating the above procedure.

Perform the above test for nitrite on a spot plate using the solution after the removal of nitrite. No red colouration at this stage indicates complete removal of nitrite. Now add a small quantity of Zn-dust and stir with a glass rod. Red colouration at this stage indicates **nitrate**.

(4) Chloride (Cl^-), Bromide (Br^-) & Iodide (I^-) in Mixture

Take 2-3ml of the neutralized Na_2CO_3 extract in a centrifuge tube, acidify with HNO_3 , and add drops of AgNO_3 solution. If a precipitate is formed, add more AgNO_3 solution until precipitation is complete. Centrifuge, and wash the precipitate with a little water.



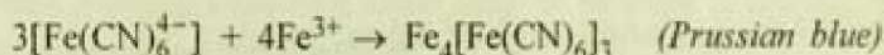


CAUTION: Discard the ammoniacal solution containing $[\text{Ag}(\text{NH}_3)_2]^+$ complex immediately after test to avoid explosion. Don't throw this solution to waste paper basket to avoid fire. Pour the solution in wash basin and wash out with running water.

(5) Ferrocyanide, $[\text{Fe}(\text{CN})_6]^{4-}$, Ferricyanide $[\text{Fe}(\text{CN})_6]^{3-}$ & Thiocyanate $[\text{SCN}^-]$ in Mixture

Spot a Whatman No. 1 filter paper strip with a drop of acidified FeCl_3 solution and dry the paper. Add a drop of the test solution on the spot using a capillary tube. If a dark coloured spot is produced, hold a solution of dilute (2M) HCl on the spot with the aid of a capillary dropper. The spot gradually separates into three zones. A central deep blue (Prussian blue) spot due to $[\text{Fe}(\text{CN})_6]^{4-}$, a red ring of $[\text{Fe}(\text{SCN})_2]^{2+}$ moving outwards due SCN^- and a green zone in between due to $[\text{Fe}(\text{CN})_6]^{3-}$ ion.

Reactions:



Mixing of Prussian blue colour due to $\text{Fe}_4^{III}[\text{Fe}^{II}(\text{CN})_6]_3$ and brown colour due to $\text{Fe}^{III}[\text{Fe}^{III}(\text{CN})_6]$ on the filter paper produces a green colouration in the middle zone.

(6) Bromide (Br^-) & Iodide (I^-) in Mixture

Take ~1 ml of the neutralized Na_2CO_3 extract in a test tube, add ~1 ml of CCl_4 or CHCl_3 , 1-2 drops of Cl_2 -water and shake. A violet organic layer (due to I_2) indicates iodide. To the resulting liquid, add more Cl_2 -water and shake. The violet colour of the organic layer gradually fades as I_2 is oxidized to iodic acid (HIO_3) by excess Cl_2 -water. Continue adding drops of Cl_2 -water and shaking each time. Gradually the organic layer becomes brown coloured as bromide is oxidized to bromine by Cl_2 - water. Therefore,

Violet organic layer - **Iodide present.**

Brown organic layer - **Bromide present.**

If iodide is absent, only the brown colour due to bromine appears on addition of Cl_2 -water.

(7) Iodate & Iodide in Mixture

Liberation of iodine on acidification of the Na_2CO_3 extract, indicates iodide and some oxidizing agent, one of which may be iodate.

Silver iodide, AgI , ($K_{sp} = 8.3 \times 10^{-17}$) is much less soluble than silver iodate, AgIO_3 ($K_{sp} = 3.1 \times 10^{-8}$). So when a small amount of soluble silver salt is added to a solution containing both iodate and iodide, yellow precipitate of AgI appears first, leaving much of the iodate in solution. This separation is more facilitated if instead of adding a soluble silver salt, like AgNO_3 , a sparingly soluble silver salt, such as, Ag_2SO_4 ($K_{sp} = 1.6 \times 10^{-5}$), that is more soluble than both AgI and AgIO_3 , is added. After separation of AgI by filtration (or centrifugation), the solution may contain iodate and an excess of unreacted Ag_2SO_4 . If iodate is now reduced to iodide by treatment with SO_2 - water (cf. Sect. 5.15), AgI is again precipitated. But if SO_2 - water is added to the solution in presence of Ag^+ ions, the test is interfered due to precipitation of silver sulfite, Ag_2SO_3 .

Unreacted Ag^+ ions may be removed by precipitation of silver carbonate (Ag_2CO_3) by treating the test solution with 0.5M sodium carbonate solution. After removal of Ag_2CO_3 by centrifugation (or, filtration), the solution is just acidified with dil. 2M HNO_3 , CO_2 is boiled off and then treated with SO_2 - water, when iodate is reduced to iodide. Excess SO_2 is to be expelled by boiling. The resulting solution should be made distinctly acidic with 2M HNO_3 and treated with 0.1M silver nitrate solution, when yellow precipitate of AgI appears. The yellow precipitate is insoluble even in conc- NH_3 . Yellow precipitate at this stage indicates iodate.

The flow diagram of the procedure is given below:

Iodate (IO_3^-) & Iodide (I^-)

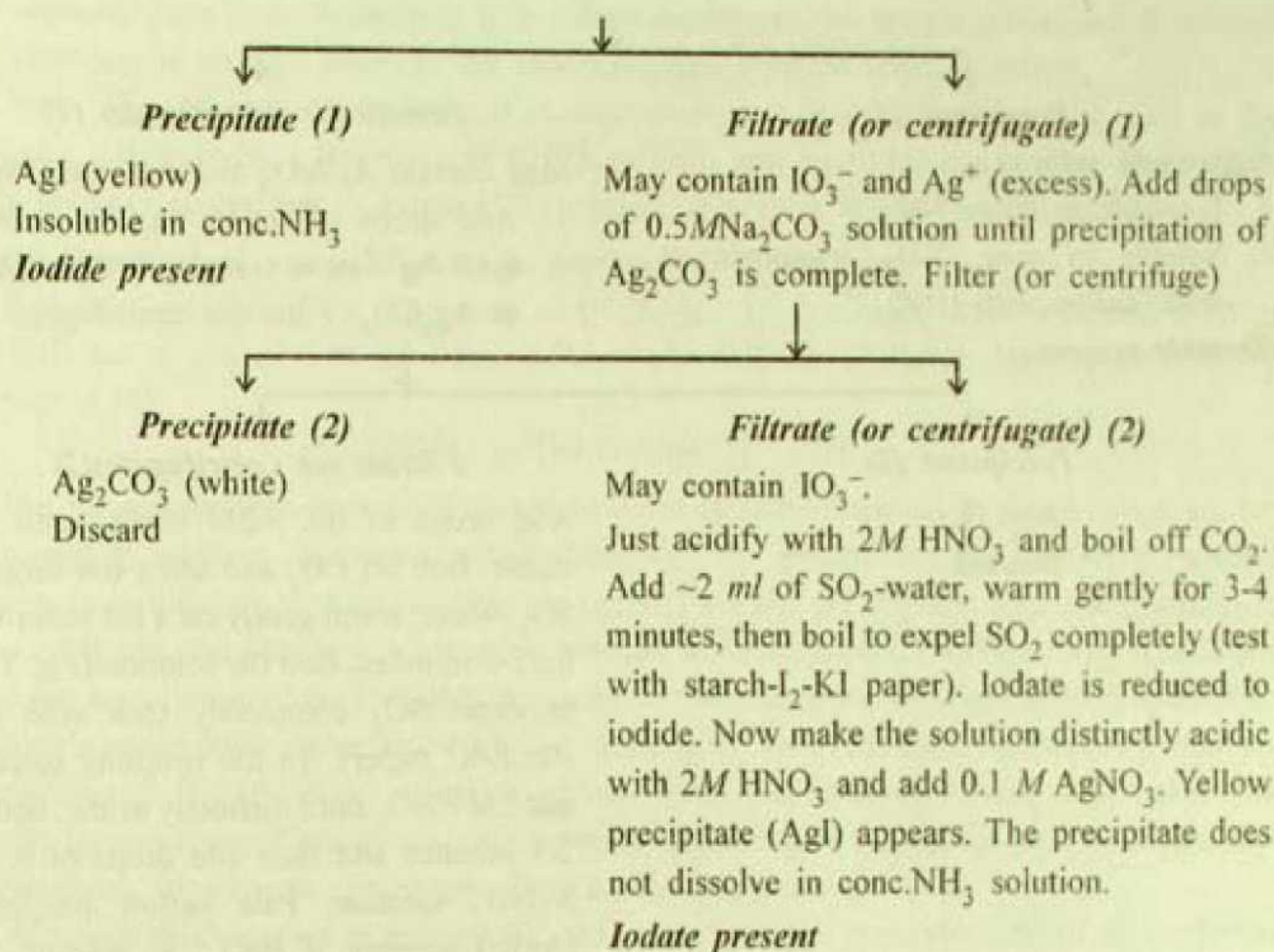
(Neutralized Na_2CO_3 -extract)

(i) To 1-2 drops of the neutralized Na_2CO_3 extract in a test tube add ~0.5ml of CCl_4 or CHCl_3 , add 1-2 drops of dil. 2M HNO_3 or HCl and shake. Violet colour in the organic layer indicates the presence of iodide and some oxidizing agent, one of which may be iodate.

(ii) If iodine is not liberated in test (i), either iodide is absent, or any oxidizing agent, or both may be absent. Add 1-2 drops of Cl_2 - water and shake. If iodine is now liberated, iodide is present, but oxidizing agents, like iodate, may be absent.

(iii) If test (i) is positive, proceed as follows:

Take 2-3 ml of the neutralized Na_2CO_3 extract in a test tube, add a saturated solution of Ag_2SO_4 until precipitation is complete. Warm gently for 1-2 minutes and filter (or, centrifuge).



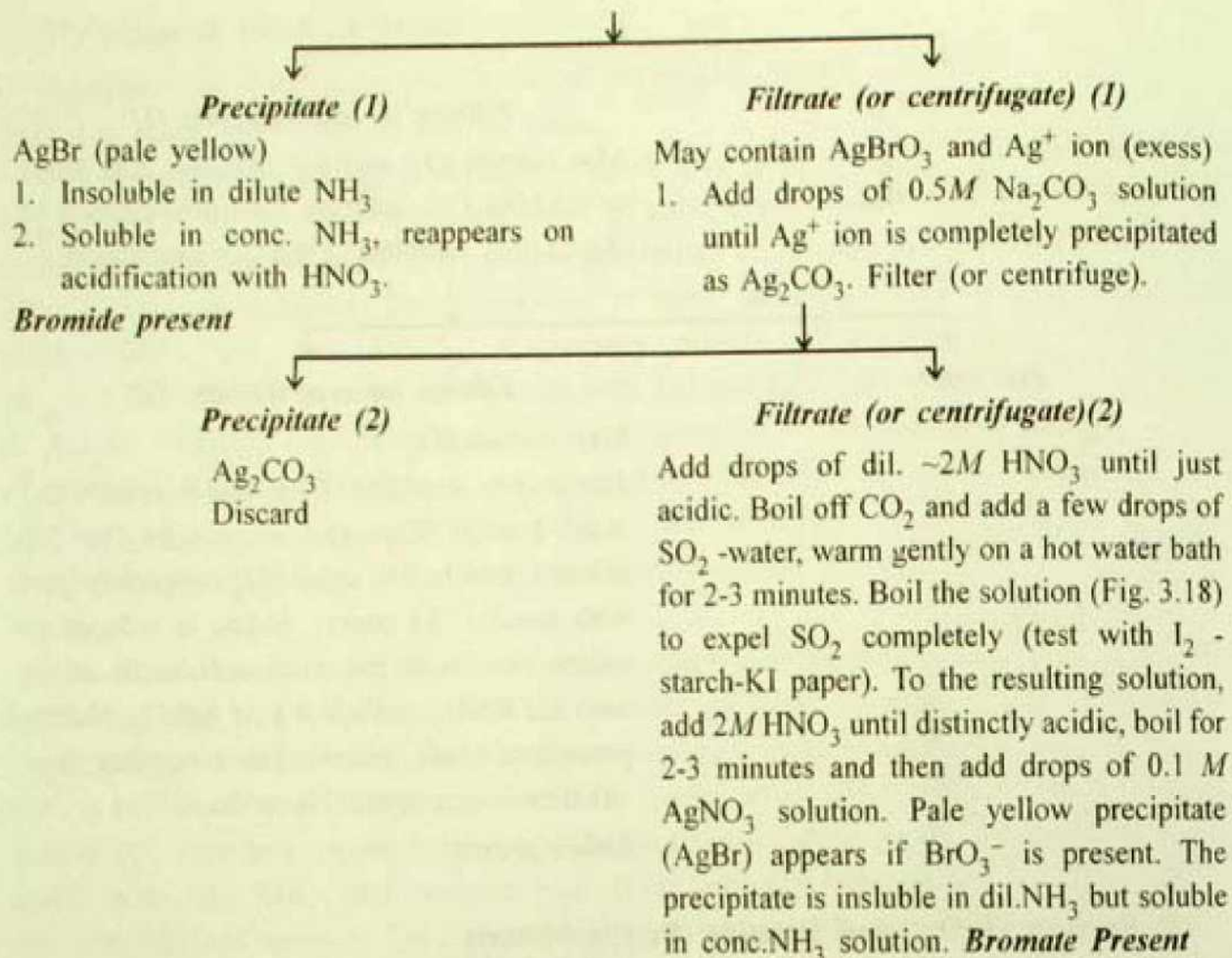
(8) Bromate (BrO_3^-) and Bromide (Br^-) in Mixture

If bromide and a strong oxidizing anion such as bromate is present, the Na_2CO_3 extract becomes brown coloured on acidification.

Silver bromide, AgBr , ($K_{sp} = 4.9 \times 10^{-13}$) is much less soluble than silver bromate, AgBrO_3 ($K_{sp} = 5.2 \times 10^{-5}$). So, when AgNO_3 solution is added to a solution containing a mixture of bromate and bromide, AgBr is first precipitated, whereas, most of the AgBrO_3 remains in solution. The filtrate after separation of AgBr by centrifugation or by filtration, followed by removal of excess Ag^+ ion as AgCO_3 by treating with $0.5M \text{Na}_2\text{CO}_3$ solution and after removal of unreacted carbonate as CO_2 by acidification and boiling, is treated with SO_2 -water, which reduces BrO_3^- to Br^- (cf. Sect. 5.14). On addition of AgNO_3 to this reduced solution after removal of SO_2 , pale yellow precipitate of silver bromide appears, which is soluble in conc.NH_3 . A flow diagram of the procedure is given below:

(BrO_3^-) & (Br^-) in Mixture (Neutralized Na_2CO_3^- extract)

1. Take 2-3 ml of the neutratised Na_2CO_3 extract, add dil. $2M \text{HNO}_3$ until distinctly acidic.
2. Add drops of $0.1 M \text{AgNO}_3$ solution. If a precipitate appears, add more AgNO_3 solution until precipitation is complete. Filter (or centrifuge).

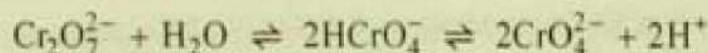


CAUTION: Discard the ammoniacal solution containing $[\text{Ag}(\text{NH}_3)_2]^+$ into the wash basin and wash out with running water immediately after test to avoid explosion.

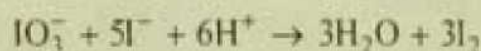
(9) Monochromate (CrO_4^{2-}) and Dichromate ($\text{Cr}_2\text{O}_7^{2-}$) in mixture

(a) Detection of dichromate in presence of monochromate

Dichromate solution is weakly acidic due to hydrolysis,



whereas, monochromate solution is weakly alkaline (cf. Sect. 5.18). Aqueous solution of dichromate, however, can supply sufficient H^+ ions as required for oxidation of iodide to iodine by iodate ion:



Monochromate is without effect in this reaction. This forms the basis of detection of dichromate in presence of monochromate.

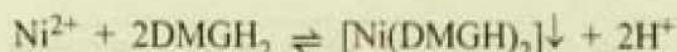
Place one drop of the test solution, or, a grain of the solid sample containing a mixture of dichromate and monochromate in a cavity of a spot plate. In another cavity of the spot plate, take a drop of K_2CrO_4 solution or a grain of solid K_2CrO_4 . Add 1 drop of freshly prepared 5% $\text{KI} - \text{KIO}_3$ solution and 1 drop of starch indicator to each of these cavities. Stir with

two separate glass rods. A Distinct blue colour appears in the sample cavity in ~5 minutes if dichromate is present, whereas, the monochromate solution remains yellow.

Note: The test may be carried out in semi-micro test tubes. Starch may be used as the indicator. Alternatively a few drops of CHCl_3 or CCl_4 may be added and shaken. The organic layer becomes violet due to iodine if dichromate is present in the test sample.

(b) Detection of monochromate in presence of dichromate

Red coloured crystalline precipitate of $[\text{Ni}(\text{DMGH})_2]$ is formed when a neutral solution of Ni(II) salt is treated with an excess of alcoholic solution of dimethylglyoxime (DMGH_2 , cf. Sect. 4.15):



But the precipitation remains incomplete if the H^+ ions liberated in this reaction are not consumed by addition of a base, viz. aq-NH_3 , and the precipitated $[\text{Ni}(\text{DMGH})_2]$ complex remains in equilibrium with its constituents, i.e. Ni^{2+} ion and the DMGH_2 ligand. If this mixture is now filtered, the filtrate is a saturated solution of the complex, $[\text{Ni}(\text{DMGH})_2]$. The above solubility equilibrium of the $[\text{Ni}(\text{DMGH})_2]$ complex may be disturbed (right shifted) by addition of soluble or insoluble materials which can consume H^+ ions (i.e. basic substances), when red precipitate of $[\text{Ni}(\text{DMGH})_2]$ complex comes down immediately. Thus, this nickel (II)-dimethylglyoxime equilibrium mixture maybe used as a reagent for testing basic materials, such as carbonate, bicarbonate, phosphate, borate, monochromate etc.

Although this reaction is not specific for monochromate, it maybe applied as a selective test for detecting monochromate in presence of dichromate, since monochromate can consume the H^+ ions and is converted to dichromate.



But dichromate does not consume H^+ ions, and shows no action with this reagent.

Reagent : Nickel (II) - dimethylglyoxime equilibrium solution.

Dissolve ~0.28g of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (or, corresponding amount of any soluble Ni(II) salt in 30 ml of water (solution-A). Dissolve ~0.25 g of dimethylglyoxime in 30 ml of 95% alcohol (solution-B). Add solution-A to solution-B with vigorous stirring. Red precipitate of $[\text{Ni}(\text{DMGH})_2]$ complex starts appearing. Allow the suspension to stand for 30 minutes and then filter. Use the clear filtrate for the tests. The reagent keeps for several weeks if it is stored in a stoppered bottle. If any red precipitate appears, filter it off and use the clear filtrate for the tests.

Take a drop of the concentrated test solution, or, a grain of the solid test sample containing monochromate and dichromate in a cavity of a spot plate. In another cavity of the spot plate, take a drop of concentrated solution of $\text{K}_2\text{Cr}_2\text{O}_7$. Add one drop of the Ni(II)-dimethylglyoxime-equilibrium solution to each of these cavities and stir with two separate glass rods. Red precipitate of $[\text{Ni}(\text{DMGH})_2]$ complex appears in the sample cavity if it contains monochromate. No precipitate is observed in the dichromate cavity.

Limit of identification: 18γ of K_2CrO_4 in presence of 5000γ of $\text{K}_2\text{Cr}_2\text{O}_7$.

7.5 Interfering Anion Radicals and Their Removal / Elimination

The following anions, if present in the sample, interfere in the systematic group separation of cation radicals (*cf.* Sect. 7.7). So, before proceeding to systematic group separation for cation analysis (*cf.* Sect. 7.8) the presence or absence of these anions is to be ensured. If any of these anions is present, it has to be removed or eliminated from the test solution at the appropriate stage to avoid its interfering actions.

(1) Phosphate (PO_4^{3-})

(a) *Interfering actions*

Phosphates of most metals ions other than the alkali metal, ammonium salts, are sparingly soluble in water, but soluble in dilute mineral acids. Phosphate ion, thus, does not interfere the separation or detection of metal ions in acidic medium, i.e., in case of Group-I and Group-II separations. On passing from Group-II to Group-III A, as the solution is made ammoniacal, phosphates along with basic salts as well as hydroxides of the metal ions of Groups III A to V (Mg^{2+}) are precipitated together, obscuring the separation of cations into groups.

Therefore, phosphate, if present, should be removed after separation of Group-II metals i.e., before making the solution ammoniacal with $\text{NH}_4\text{Cl-NH}_3$ for Group-III A precipitation.

(b) *Phosphate removal*

(i) *FeCl_3 Method*

(1) Take the filtrate after complete precipitation of Group-II metal sulfides with ($\text{HCl}+\text{H}_2\text{S}$ -water). Boil off H_2S (test with lead acetate paper). If no precipitate appears with ($\text{HCl}+\text{H}_2\text{S}$ -water), Group-II metals are absent. Then discard the solution and take a fresh portion of the sample solution and proceed.

(2) Take 1-2 drops of the test solution, add 1-2 drops of conc. HNO_3 and ~0.5-1 ml of ammonium molybdate reagent in a semi-micro test tube. Warm gently on a hot water bath. If a canary yellow precipitate appears, phosphate is present, otherwise, pass on to Group-III A separation. But if phosphate is present, proceed as follows:

(3) Take ~2-3 ml of the test solution in a small (~50 ml) beaker, add a few drops of Br_2 water or H_2O_2 (6%) or conc. HNO_3 , warm gently (to oxidize any Fe^{II} to Fe^{III}). Add ~0.5g of NH_4Cl . Heat to boiling and add drops of dilute (1:1) aq- NH_3 solution until faintly ammoniacal. If no turbidity appears, metals of Group-III A, IIIB, IV, V (Mg^{2+}) are absent. Then search for Na^+ and K^+ ion only. But if a turbidity appears, which may be hydroxides of Fe^{III} , Cr^{III} , Al^{III} and Mn^{IV} (by aerial oxidation), then proceed as follows:

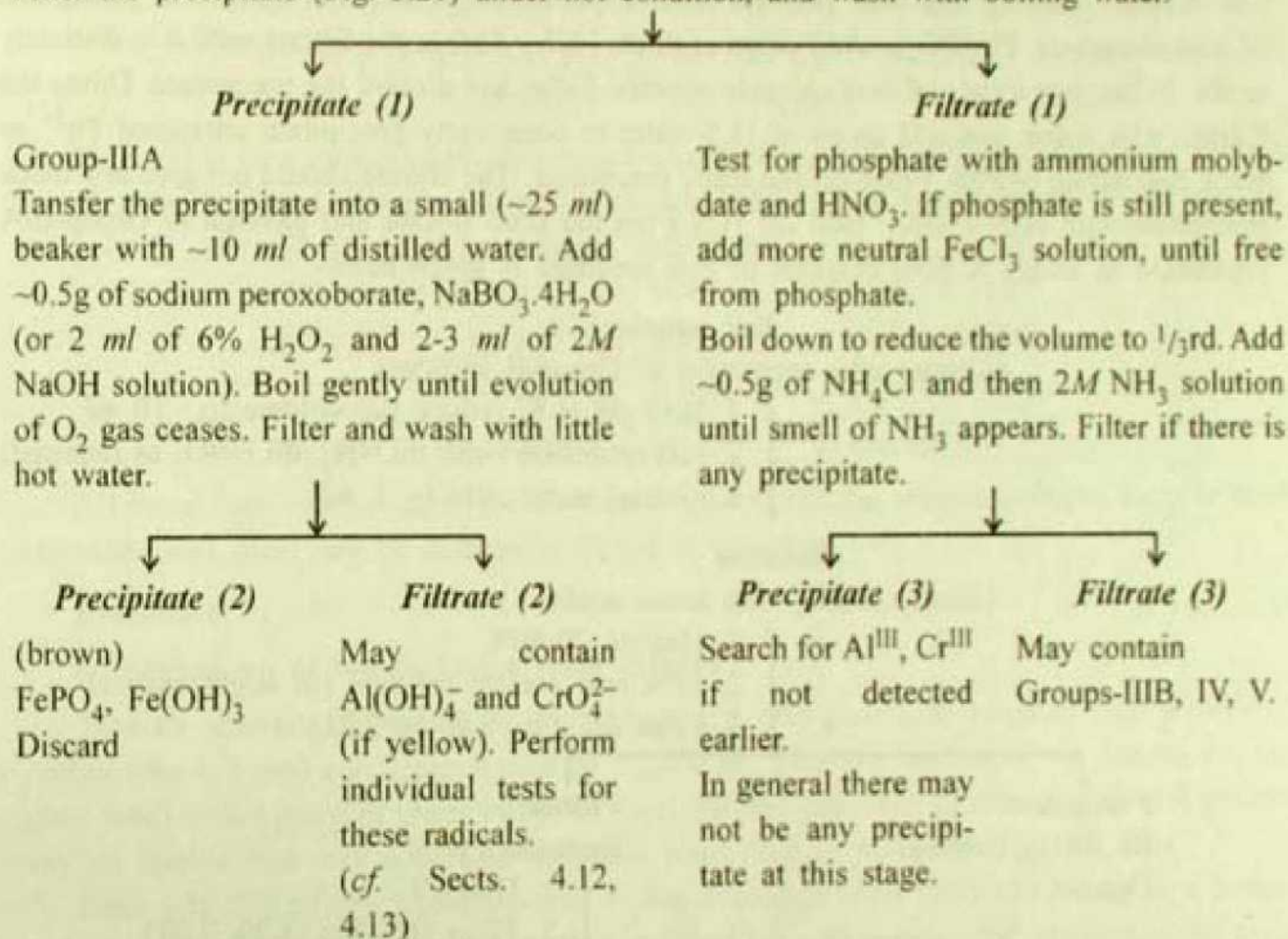
(4) Dissolve the turbidity by adding drops of just sufficient amount of dilute (~2M) HCl solution (avoiding excess). To test whether iron is present, place 1 drop of the solution on a spot plate, add 1 drop of (1:1) HCl and 1 drop of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution. Intense blue colouration indicates the presence of iron in the sample. Then proceed as follows:

(5) Heat the main bulk of the solution to boiling.

Add drops of very dilute aq- NH_3 again until a faint but permanent turbidity just appears

or the solution is just ammoniacal. Test with red litmus paper. Add with stirring 2-3 ml of 9M acetic acid and 5 ml of 6M ammonium acetate (pH ~4.8 buffer) solution. Filter any precipitate formed at this stage and search for Group-III A metals in this precipitate.

(6) If the colour of ammoniacal test solution is red-brown, sufficient Fe^{III} is present in the solution to combine with phosphate ions. If the colour of the solution is not red-brown, add drops *neutral FeCl_3 solution** with stirring until the solution acquires a red-brown colour. Dilute the mixture with water to ~25 ml. Boil gently with stirring for ~25 minutes. Reddish brown precipitate [of phosphates and basic acetates of Fe^{III} , Al^{III} , Cr^{III} and of $\text{Fe}(\text{OH})_3$] appears. Filter the precipitate (Fig. 3.21) under hot condition, and wash with boiling water.



(ii) Phosphate removal by lead acetate method

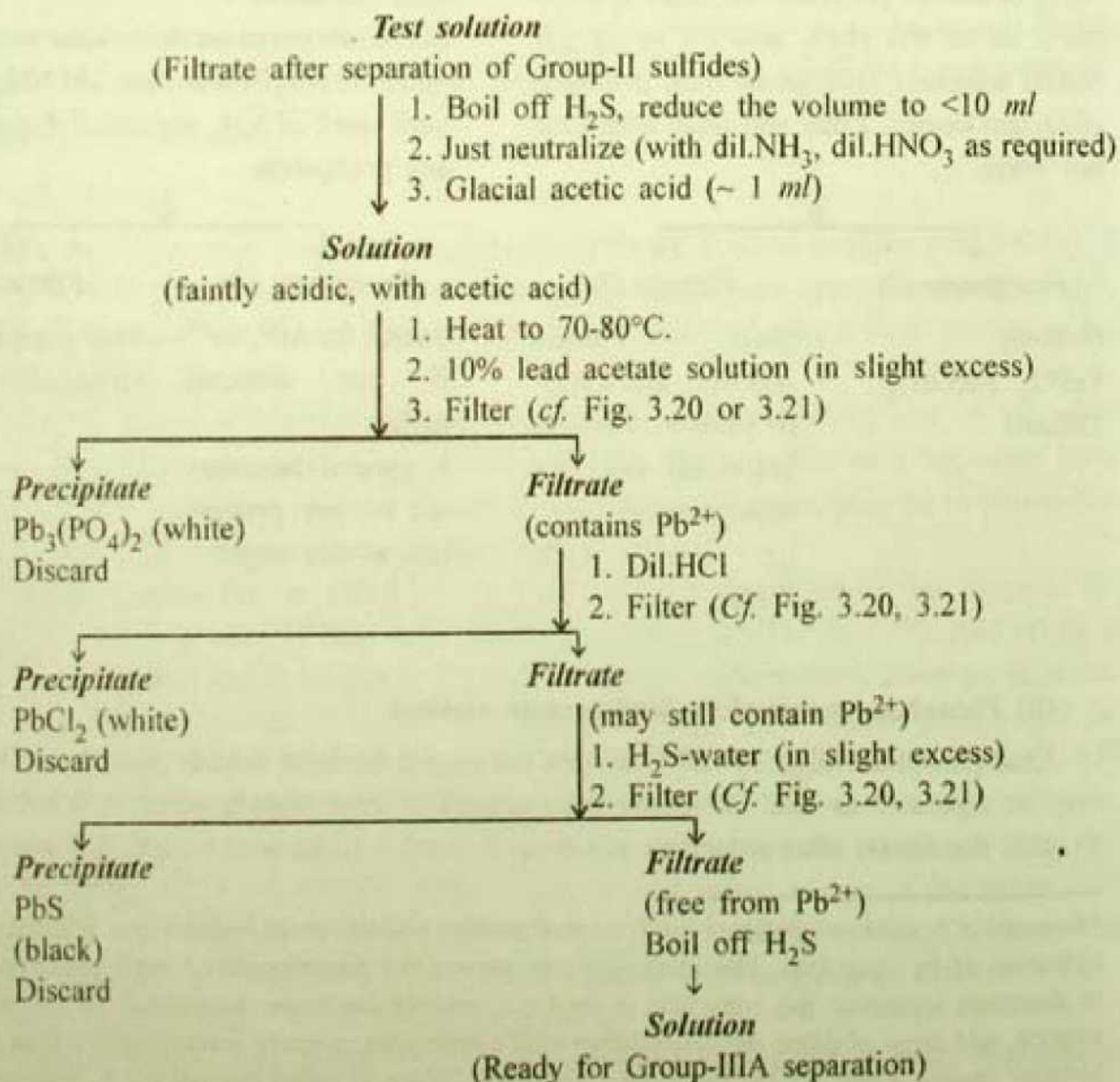
Lead phosphate ($K_{sp} = 7.9 \times 10^{-43}$ at 25°C) is among the least soluble phosphates. Phosphate may be separated as lead phosphate from neutral or even weakly acidic test solution.

Boil the filtrate after separation of Group-II metal sulfides to drive off H_2S and to reduce

**Neutral FeCl_3 solution*: Ordinary FeCl_3 reagent solution contains much hydrochloric acid for preventing hydrolysis of $\text{Fe}^{3+}(\text{aq})$ ions. This extra acid may prevent the precipitation of ferric phosphate. For use in phosphate separation this extra acid in the FeCl_3 solution has to be neutralized. To 2-3 ml of FeCl_3 solution, add drops of dilute aq-NH_3 solution until a red-brown coloured solution with a faint permanent turbidity results. Filter off the precipitate. The clear filtrate is called *neutral FeCl_3 solution*.

the volume to less than 10 ml. Add drops of (1:1) aq-NH₃ solution to have a just neutral or faintly alkaline solution (test with litmus papers).

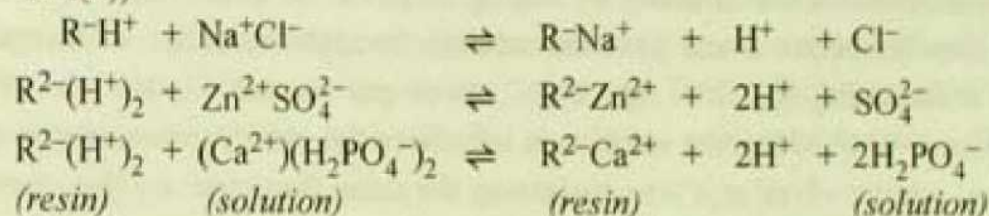
Add drops of very dilute HNO₃ and stir with a glass rod until turbidity if any is just dissolved (avoid excess HNO₃). Add ~1 ml of glacial acetic acid and warm gently to 70-80°C. Add drops of 10% lead acetate solution with constant stirring with a glass rod, providing a slight excess of the reagent to ensure complete precipitation of phosphate as lead phosphate. Allow to stand for ~20 minutes. Check the completeness of precipitation of phosphate by adding 1-2 drops of the lead acetate solution to the supernatant liquid. Allow to stand for another ~30 minutes. [during this time perform other experiments]. Filter and discard the precipitate of lead phosphate, Pb₃(PO₄)₂. Add drops of dilute HCl (~5M) to the filtrate until it is distinctly acidic. White precipitate of lead chloride appears. Filter and discard the precipitate. Dilute the filtrate with water and add drops of H₂S-water to completely precipitate unreacted Pb²⁺ as black precipitate of PbS. Filter off the black precipitate. The filtrate should not give any black precipitate with H₂S - water. Boil off H₂S from the final filtrate and pass on to Group-IIIa separation as usual. A flow diagram of this procedure is given below.



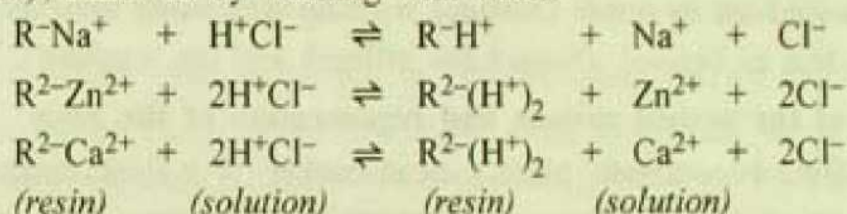
(iii) Phosphate Removal by Ion-Exchange Method

Principle

When weakly acidic solutions containing metal salts including phosphates are passed through a column of strongly acidic cation exchange resin in H^+ -form ($R-H^+$), the metal ions exchange with equivalent amounts of H^+ ion and remain held up (*sorbed*) in the resin column. The anions of the metal salts as well as neutral molecules pass out of the resin column as effluent (*cf.* Sect 2.5.(b))



Thus, all anions including phosphate are separated from the cations. The sorbed cations may now be displaced (*desorbed*) from the resin column by passing a solution of HCl through the column (*elution*), followed by washing with water.



All metal ions now occur in the combined effluent and the washings in the form of their chlorides, and they may be detected/analysed in the usual way.

Procedure

(i) Setting up of ion-exchange resin column

Take an ordinary 25 ml burette or a (15 cm × 1 cm) glass tube attached with a piece of rubber tube (~5 cm) and a pinch cock at its bottom. Plug the bottom of the burette (or the glass tube) with a piece of clean soft glass wool. Fill the tube with distilled water and remove any air bubble that may adhere to the glass wool plug or to the wall of the tube.

Place ~15-20g of dry strongly acidic cation exchange resin (200-400 mesh) in a beaker and add ~50 ml of 6M HCl, stir and allow to stand for ~30 minutes for swelling of the resin and its transformation to H^+ - form.

Introduce the resin inside the column with the help of a spatula (of Fig 3.13b) by draining out water through the stopper (or pinch cock as the case maybe). Fill the column up to its neck, keeping a gap of ~5 cm at the top for filling the sample solution. Place a piece of clean glass wool above the resin bed (*cf.* Fig. 2.9).

Now pass 15-20 ml of 6M HCl through the resin column to finally replace cations if any still present in the resin, by H^+ ions. The flow rate should be adjusted at 1-2 drops per second. Care should be taken that the resin column always remains covered with liquid. When nearly 1 ml of the acid solution remains above the top of the column, wash the column with water, adding ~5 ml at a time at the same flow rate. Continue washing with water until the washings are acid-free, i.e., no longer produce red colouration with methyl red indicator, or until the pH

of the washing is ~ 4 (check with a pH-paper or Universal indicator). The column is now ready for ion-exchange separation of cations.

(ii) Sorption of cations and separation from anions including phosphate

The test solution should not be strongly acidic. Acidity should be around $(0.03 - 0.01)M$ i.e., pH around 1.5 to 2. If the test solution is strongly acidic, evaporate the solution to almost dryness by gentle heating. Neutralize with drops of $2M NH_3$ until a faint permanent turbidity appears. Just dissolve the turbidity by adding drops of $6M HCl$. Dilute to $\sim 5-10 ml$ with water, cool to room temperature and pass the solution through the cation exchange resin column in H^+ -form maintaining the flow rate at 1-2 drops per second. Collect the effluent in a small beaker. When $\sim 1 ml$ of the test solution is left above the resin column, start washing the column with water, adding $\sim 5 ml$ at a time maintaining the same flow rate. By this operation, the cations in the test solution are held up by the resin with release of equivalent amount of H^+ ions, and the anions including phosphate, (which now exists as unionized H_3PO_4 and $H_2PO_4^-$ ion in acidic medium, since pK_a 's of H_3PO_4 are 2.12, 7.21 and 12.32), pass out of the column and are finally washed out by water. Continue washing with water until the washings are acid free (i.e., pH ~ 4 , test as before). Discard the effluent and the washings.

(iii) Elution of the sorbed cations and regeneration of the resin

After the washing is complete, place a clean beaker (or a flask) under the resin column and pass $\sim 15-20 ml$ of $6M HCl$ through it, maintaining the same flow rate (1-2 drops per second) as before. By this operation, the sorbed cations are released from the resin. Wash the column with water to remove the displaced cations and collect 3-4 washings ($\sim 30-40 ml$ in total) in the same beaker. Preserve this combined effluent and washings for analysis of cations. Continue washing the column with water, until the washings are acid free (test as before). The column is now ready for another operation.

(iv) Analysis of cations in the combined effluent and washings

Evaporate the solution almost to dryness in a **FUME CUPBOARD** by gentle boiling. Moisten the dry residue with a few drops of $6M HCl$ and dilute with water to the original volume before ion-exchange separation. Search for cations in this solution in the usual way.

(2) Fluoride (F^-), Borate (BO_3^{3-}), Boric Acid (H_3BO_3), Silicate (SiO_3^{2-}), Silicic Acid (SiO_2, xH_2O).

(a) Interfering actions

(i) Fluoride (F^-)

Fluoride ion forms sparingly soluble salts with alkaline earth metal (Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+}) and also Pb^{2+} , (U^{IV*} , Th^{IV*}) ions in ammoniacal medium. If large excess of soluble fluoride is present, it may form soluble fluoro complexes with Fe^{3+} , Al^{3+} , (Ti^{4+} , Zr^{IV})* and keep them in solution (as FeF_6^{3-} , AlF_6^{3-} , TiF_6^{2-} * etc.) and prevent their precipitation. It has to be removed before proceeding to Group-III A separation.

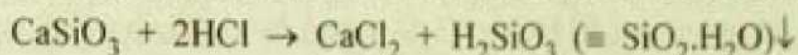
*Rare elements

(ii) Borate (BO_3^{3-}), Boric Acid (H_3BO_3)

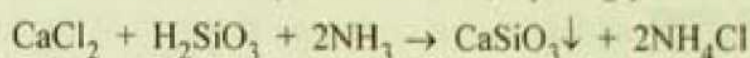
These form sparingly soluble borate salts or basic salts with most metal ions (except Na^+ , K^+ , NH_4^+) in ammoniacal medium and obscure systematic Group-separation. These should be removed before proceeding to Group-IIIa separation.

(iii) Silicate (SiO_3^{2-}) and Silicic Acid ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$)

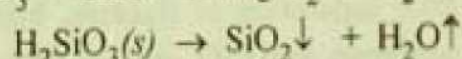
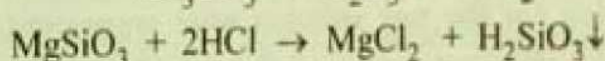
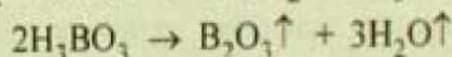
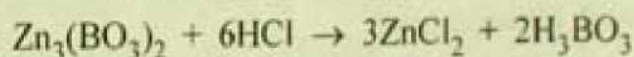
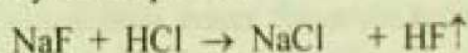
Silicic acid ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$) forms colloidal solution with water. It dissolves partly on boiling with hydrochloric acid during preparation of solution for detection of cation radicals. But soon starts precipitating, as the solution is cooled on standing. This turbidity continues in the subsequent steps of analysis. Silicate salts dissolve in mineral acids and set free silicic acid.



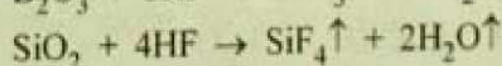
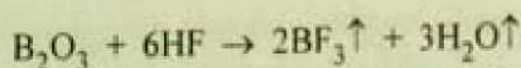
In ammoniacal medium (i.e., Group-IIIa onwards), sparingly soluble silicates precipitate out.



This is how systematic group separation is obscured in presence of F^- , BO_3^{3-} (H_3BO_3) and SiO_3^{2-} ($\text{SiO}_2 \cdot x\text{H}_2\text{O}$). These radicals should be removed, better prior to entering into group separation. It is, however, much easier to remove these interfering anion radicals, than the removal of the phosphate radical. These are conveniently removed by digesting the original solid sample with concentrated hydrochloric acid and repeated evaporation to dryness. Fluorides are removed as volatile hydrogen fluoride. Borates are transformed to boric acid, which undergoes dehydration and volatilizes out. Silicates are transformed to silicic acid, which is dehydrated to granular silica by this operation.



If fluoride is also present along with borate (boric acid) and or silicate (silicic acid), removal of these anion radicals is facilitated due to the formation of volatile BF_3 and or SiF_4 as the case may be.



(b) Procedure of removal

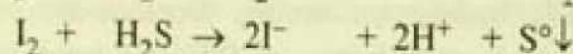
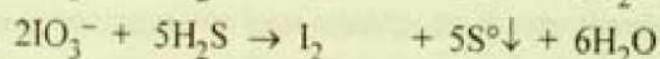
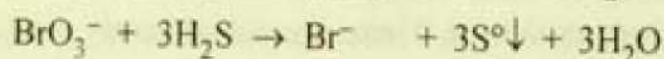
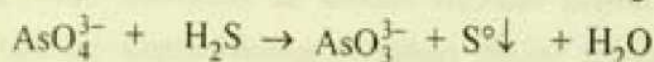
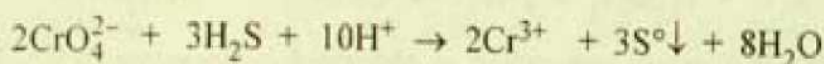
Take a small amount (~ 0.2 g) of the solid sample in a small beaker or in a porcelain crucible add $\sim 0.5 - 1$ ml of conc. HCl and heat gently inside a **FUME CUPBOARD** or using the apparatus as in (Fig. 3.17) until evaporated to dryness. Cool and moisten the residue with a few drops of conc. HCl and evaporate again to dryness as before. Repeat this operation 2-

3 times. Continue heating gently while triturating the solid mass with a glass rod. This helps dehydration of silicic acid. Continue this process of baking for nearly 10 minutes. Cool and add 2-3 ml of dil.HCl, boil gently for ~2 minutes, filter under hot condition. Residue if any, may contain SiO_2 along with other acid insoluble substances in the sample. The filtrate is ready for systematic group separation starting from Group-II.

(3) Chromate (CrO_4^{2-}), Dichromate ($\text{Cr}_2\text{O}_7^{2-}$), Arsenate (AsO_4^{3-}), Bromate (BrO_3^-) Iodate (IO_3^-).

(a) Interfering actions

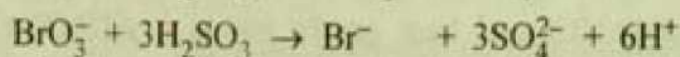
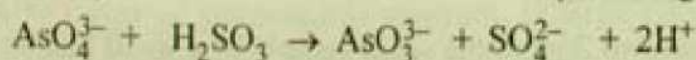
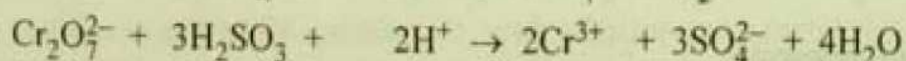
These anion radicals act as oxidizing agents in acid medium. They interfere in the separation of Group-II metal sulfides with (dil.HCl + H_2S -water) by oxidizing H_2S with precipitation of sulfur, which is separated in milky colloidal form, that is difficult to filter, as it even passes through the finest filter paper.



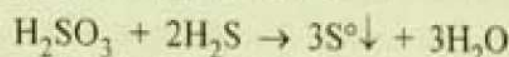
These anion radicals, if present in the sample solution for group analysis, should be reduced before proceeding to separation of Group-II metal sulfides.

(b) Procedure of removal (elimination)

Chromate, dichromate, arsenate and other oxidizing agents are conveniently reduced by treating the HCl test solution [or the test solution after separating Group-I (Ag^+ , Hg^+ , Pb^{++}) chlorides or the test solution after separation of fluoride, borate (boric acid), silicate (silicic acid) as the case may be] with sulfurous acid (SO_2 -water). CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ are reduced to green Cr^{III} salt. AsO_4^{3-} is reduced to arsenite (AsO_3^{3-}). Bromate (BrO_3^-) is reduced to bromide (Br^-) and iodate (IO_3^-) is reduced to iodide (I^-)



Since H_2SO_3 is oxidized to sulfate (SO_4^{2-}) ion by these reactions, if the metal ions viz, Pb^{2+} , Ba^{2+} , Sr^{2+} , also Ca^{2+} are present in the sample solution, they may precipitate at this stage as their sulfates. Therefore, if any white precipitate appears on treatment with H_2SO_3 , filter the mixture and search for Pb^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} in the precipitate by their individual tests (cf. Sect 7.9), then pass on to Group-II separation with the filtrate after removing the unreacted H_2SO_3 by boiling the solution in the **FUME CUPBOARD** or using the apparatus as in Fig. 3.17. Removal of H_2SO_3 is necessary at this stage, since H_2SO_3 itself can oxidize H_2S with separation of colloidal sulfur,



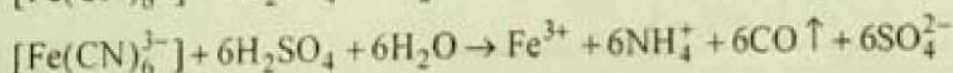
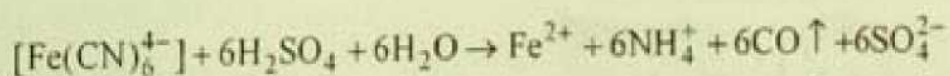
Complete removal of SO_2 (i.e. $\text{H}_2\text{SO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{SO}_2$) may be ensured by boiling the solution and testing the issuing vapour with blue coloured starch-iodine-iodide paper (cf. Figs. 3.27, 3.29). Discharge of blue colour by the issuing vapour indicates the presence of dissolved SO_2 in the solution. Proceed to Group-II separation when the blue colour of starch-iodine-iodide paper is not discharged by the issuing vapour.

(4) Ferrocyanide [$\text{Fe}(\text{CN})_6^{4-}$], Ferricyanide [$\text{Fe}(\text{CN})_6^{3-}$], and Thiocyanate (SCN^-)

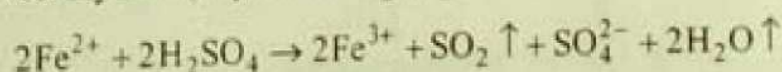
(a) Interfering actions

Ferrocyanide and ferricyanide of Ag, Hg, Pb, Cu, Cd, Fe, Co Ni, Zn (also Mo, U)* are sparingly soluble and those of Fe, Cu, Co, Ni (Mo, U)* are intensely coloured. Thiocyanates of Ag, Cu, Hg, Pb are also sparingly soluble. More over, thiocyanate ion forms intensely coloured soluble complexes with Fe^{3+} (blood red coloured [$\text{Fe}(\text{SCN})^{2+}$]) and Co^{2+} (intense blue coloured $\text{H}_2[\text{Co}(\text{SCN})_4]$). As such, these anion radicals interfere in the systematic group separation of cation radicals right from Group-I and should be removed before proceeding into group separation. The most convenient method of removing these interfering anions is to decompose them by heating with conc. H_2SO_4 . **[CAUTION : POISONS]**.

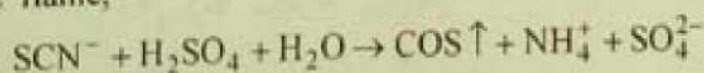
Ferrocyanide and ferricyanide are decomposed by hot conc. H_2SO_4 with evolution of carbon monoxide gas, which burns with a blue flame. Iron in these anions is ultimately converted to ferric sulfate.



A little sulfur dioxide may also be produced, due to oxidation of Fe^{2+} ion, produced from decomposition of ferrocyanide, by conc. H_2SO_4 ,



Thiocyanate reacts violently with hot conc. H_2SO_4 producing carbonyl sulfide (COS) that burns with a blue flame,



*Rare elements

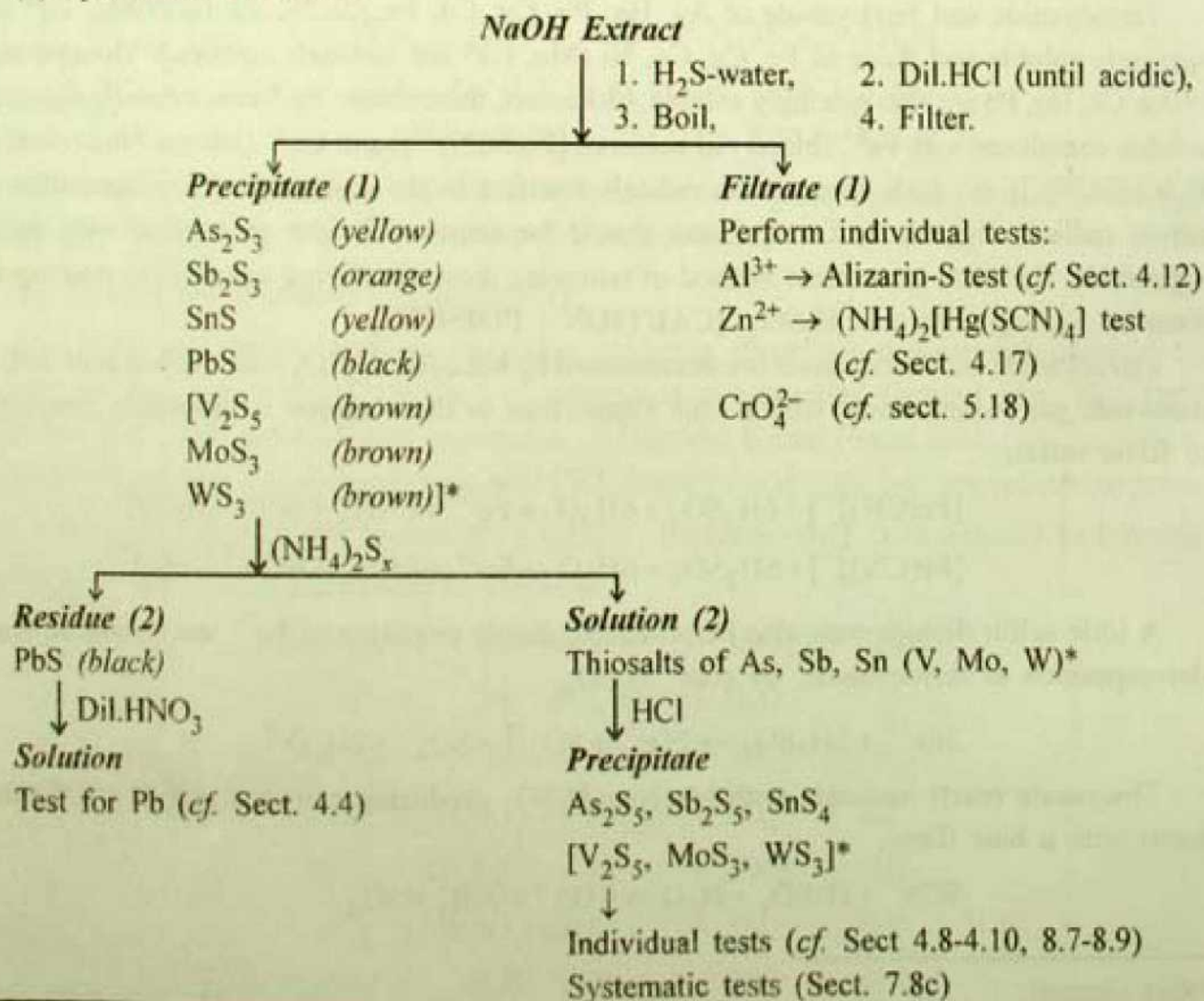
(b) Procedure of removal (elimination)

Take a small quantity (~0.2g) of the solid sample in a porcelain crucible, moisten with a few drops of conc. H_2SO_4 and heat gently inside a **FUME CUPBOARD**. Copious fumes (**CAUTION: DEADLY POISONONS**) consisting of CO , SO_2 , SO_3 (due to dehydration of $\text{H}_2\text{SO}_4 \rightarrow \text{H}_2\text{O}\uparrow + \text{SO}_3\uparrow$), COS etc, as the case may be, appear. Fluoride, chloride, bromide, iodide, nitrate, nitrite, sulfide, thiosulfate etc. are all decomposed by this treatment with evolution of volatile products eg, HF , HCl , HBr , HI and I_2 , NO_2 , NO , SO_2 etc. as the case may be.

Continue heating until the fumes subside. Cool the residual mass to room temperature and take up with little water (~4-5 ml). Filter if necessary. The residue, if any, will contain the sparingly soluble sulfates of Pb , Ba , Sr , Ca and also the constituents of the sample that are unattacked by hot conc. H_2SO_4 (e.g. SiO_2 etc.). These may be detected by their individual tests (cf. Sect 7.9). The filtrate is now ready for detection of cation radicals either by spot tests or by systematic group separation right from Group-I. If ferrocyanide and or ferricyanide are present, the test solution at this stage will contain Fe^{3+} , which should be confirmed by its usual tests (cf. Sect. 4.11) or to be separated in Group-IIIA and confirmed accordingly.

7.6 Detection of Radicals in the NaOH Extract-G

(a) Systematic Procedure



*Rare elements

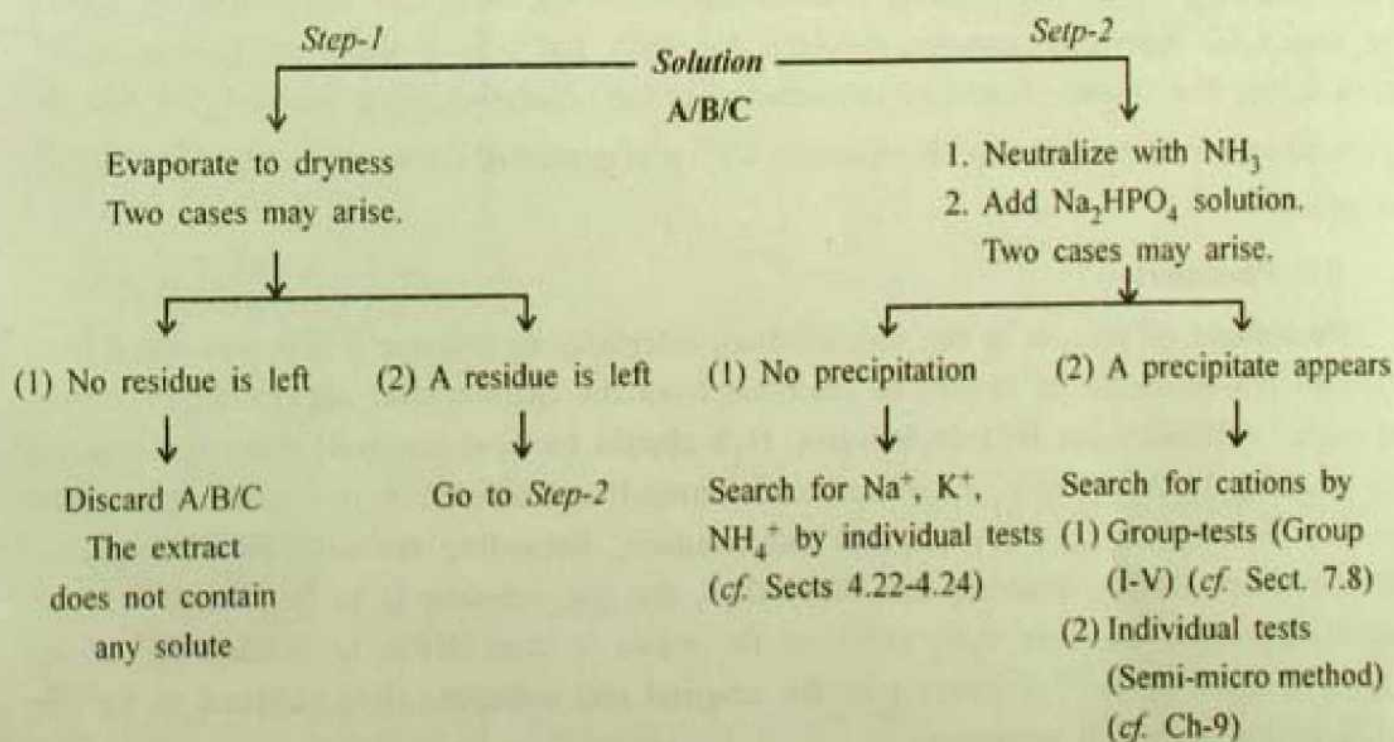
(b) Individual tests

NaOH extract may contain mainly the metal ions which form amphoteric oxides, that behave as acids with strong bases (NaOH, KOH) and as bases with strong acids. These may be detected by individual tests as well as by systematic tests.

Metal	NaOH extracted species	Individual tests/ Reagents
Pb	PbO_2^{2-}	H_2S -water, HCl, H_2SO_4 , K_2CrO_4 , KI (<i>cf.</i> Sect. 4.4)
Al	AlO_2^-	Alizarin-S test (<i>cf.</i> Sect. 4.12)
Zn	ZnO_2^{2-}	Ammonium mercuriothiocyanate test (<i>cf.</i> Sect 4.17)
As	AsO_4^{3-} , AsO_3^{3-}	(Zn+HCl) and AgNO_3 : Gutzeit's test. (<i>cf.</i> Sect. 4.8)
Sb	SbO_4^{3-} , SbO_3^{3-}	Rhodamine-B test (<i>cf.</i> Sect. 4.9)
Sn	SnO_3^{2-} , SnO_2^{2-}	Ammonium phosphomolybdate test (<i>cf.</i> Sect. 4.10)
Rare elements (Ch-8)		
V	$\text{V}_2\text{O}_7^{4-}$, VO_3^-	H_2O_2 -dil. H_2SO_4 (<i>cf.</i> Sect. 8.7)
Mo	MoO_4^{2-}	NH_4SCN -HCl- SnCl_2 test. (<i>cf.</i> Sect. 8.8)
W	WO_4^{2-}	(i) KHSO_4 - H_2SO_4 -phenol test (Defacqz reaction) (ii) SnCl_2 , (iii) Zn/HCl - tungsten blue test. (<i>cf.</i> Sect. 8.9)

7.7 Wet Test Scheme for Detection of Cation Radicals

With Aqueous or Acid extracts: Schematic procedure



7.8 Separation of Cation Radicals into Analytical Groups

For a complete discussion on the separation of Group-I to Group-V cations it is convenient to start with the aqueous extract (A) of the sample. The HCl-extracts (B, C) will not contain the Group-I metals, as the chlorides of Group-I metals will be precipitated during HCl treatment of the sample for dissolution. The presence or absence of the interfering anion radicals should be ensured before proceeding to group separation. If any of the interfering anion radicals is present, it has to be removed (*cf.* Sect 7.5) at the appropriate stage of group separation as indicated below:

(i) Ferrocyanide, Ferricyanide & Thiocyanate

If any of these radicals is present, decompose it by heating with conc. H_2SO_4 in a **FUME CUPBOARD** as described before (*cf.* Sect 7.5) and then start with separation of Group-I. Fe^{III} will appear in Group-III A if $[\text{Fe}(\text{CN})_6]^{4-}$ and or $[\text{Fe}(\text{CN})_6]^{3-}$ are present.

(ii) Fluoride, Borate (Boric Acid), Silicate

If any of these radicals is present, remove it by repeated evaporation with conc. HCl followed by baking in a **FUME CUPBOARD** as described before (*cf.* Sect 7.5). If Group-I metals are present, these radicals should be removed from the filtrate obtained after separation of Group-I. If Group-I metals are absent, it is convenient to separate these interfering anion radicals by repeatedly treating the original solid sample with conc. HCl as described and to start group separation from Group-II with the HCl-extract of the residue.

(iii) Chromate, Dichromate, Arsenate, Bromate, Iodate

These oxidizing anions interfere right from Group-I. If any of these is present, it should be reduced by H_2SO_3 (SO_2 -water) as described before (*cf.* Sect 7.5). Residue if any should be tested for individual cations, specially for Pb^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+} etc. (*cf.* Sects 4.4, 4.18-4.20). The filtrate should be subjected to group separation from Group-I (for aqueous extract) or from Group-II (for HCl extract). Cr^{III} will appear in Group-III A if $\text{CrO}_4^{2-} / \text{Cr}_2\text{O}_7^{2-}$ is present.

(iv) Phosphate

Phosphate, if present in the test solution, interferes systematic group separation from Group-III A onwards. It should be removed from the filtrate after separation of Group-II metal sulfides with $\text{HCl} + \text{H}_2\text{S}$ -water. H_2S should be first removed from the solution by boiling. If the metals of Group-I and Group-II are absent, it is convenient to start with a fresh portion of the original test solution, discarding the solution after Group-II treatment. Before entering into Group-III A, the test solution is to be treated with an oxidizing agent, such as H_2O_2 (6%), or Br_2 -water or conc. HNO_3 to oxidize Fe^{II} if any to Fe^{III} . Even if Fe^{III} is present in the original test solution, it is reduced to Fe^{II} by H_2S in the Group-II treatment.

7.8 (a) Flow Chart for Systematic Group Separation

Test solution: (Aqueous Extract-A) (Acid Extracts B, C)



1. Remove interfering anion radicals viz,
 $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{CN})_6]^{4-}$, SCN^- , if present.



Solution

2. Heat to boiling, add dilute HCl (~2M). If a precipitate appears, add more dil. HCl until precipitation is complete. Filter in the cold condition. Wash the precipitate with cold water. (Omit this step with acid extracts B and C).



Precipitate

Group-I
 white
 AgCl
 PbCl_2
 Hg_2Cl_2

Filtrate (Groups II-V)

Decompose the oxidizing anion radicals :
 CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, BrO_3^- , IO_3^- , AsO_4^{3-} by
 treating with SO_2 -water. Remove unreacted
 SO_2 by boiling. Filter if necessary.



Precipitate

white
 Sulfates of
 Pb^{2+} , Ba^{2+} , Sr^{2+} , Ca^{2+}
 if present.

Filtrate (Groups II-V)

1. Dilute with water to adjust acidity to ~0.3M in HCl, heat to boiling.
2. Treat with H_2S -water. If a coloured precipitate is formed, add more H_2S -water to ensure complete precipitation.
3. Filter and wash the precipitate with a little H_2S -water.



Confirm by individual tests
 (cf. Sects, 4.4, 4.18-4.20)



Precipitate

Group-II
 II(A) II(B)
 HgS As_2S_3
 PbS Sb_2S_3
 Bi_2S_3 SnS
 CuS SnS_2
 CdS

Filtrate (Groups IIIA-V)

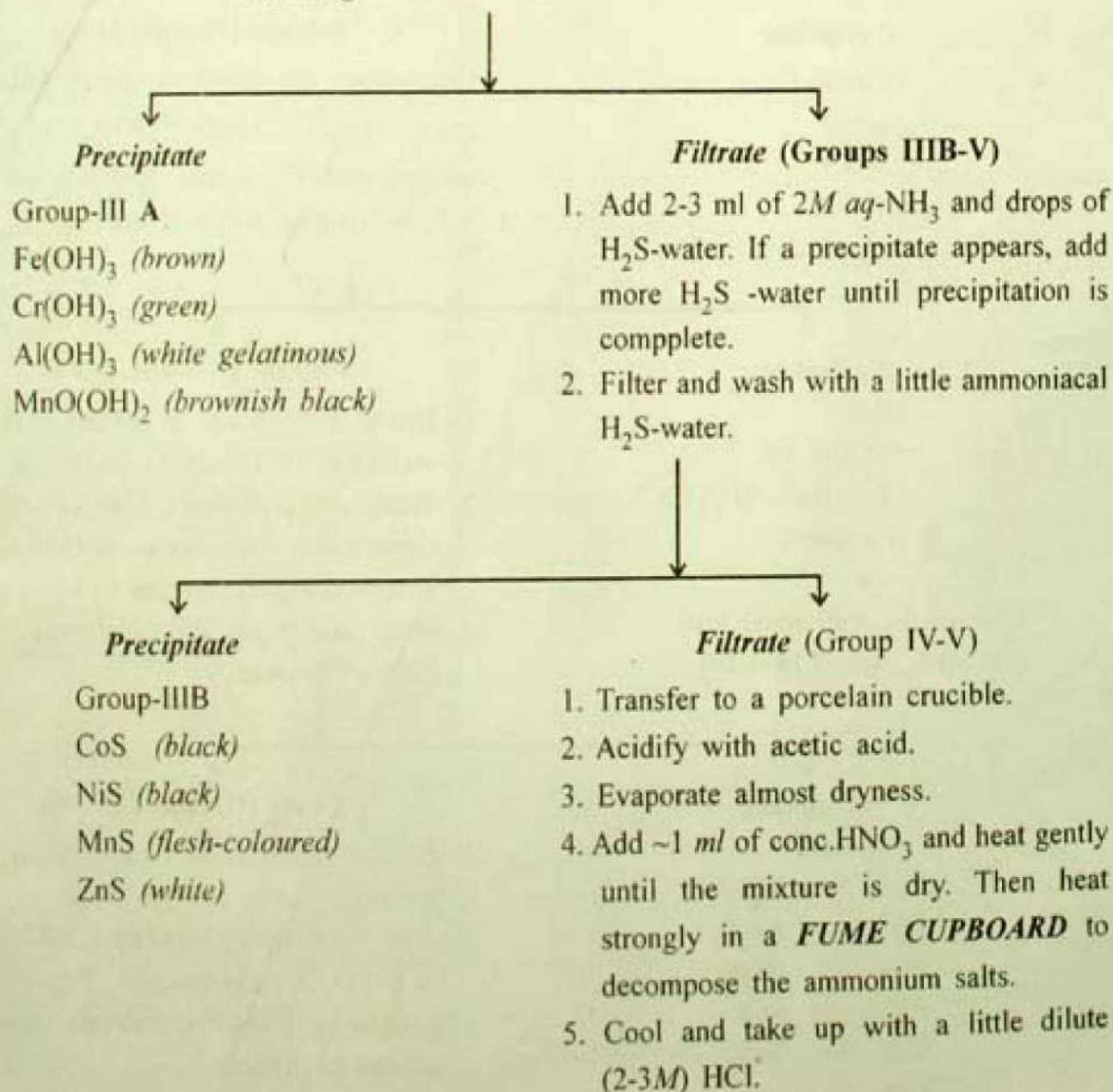
1. Boil off H_2S (test with lead acetate paper)
2. Reduce volume to ~10-15 ml.
3. Add 1-2 ml of conc. HNO_3 (or Br_2 -water or 6% H_2O_2) and boil for ~5 minutes (to oxidize Fe^{II} to Fe^{III} if present). Evaporate almost to dryness.

Filtrate (Groups IIIA-V) (contd.)

4. Remove F^- , BO_3^{3-} (H_3BO_3), SiO_3^{2-} , if present, by repeated evaporation with HCl followed by baking. Take up with little water.
5. Remove PO_4^{3-} , if present, by lead-acetate method or ferric chloride method.

If Group-I and Group-II metals and these interfering anion radicals are absent, discard this test solution and start with a fresh portion of the original test solution.

6. Add 1-2 g of NH_4Cl , heat to boiling, add 2M aq- NH_3 solution until smell of NH_3 appears, then add 1 ml in excess. Boil gently for 1 minute and filter immediately. Wash the precipitate with 1% NH_4Cl solution containing little ammonia.



If Group-I to Group-IIIB cations and the interfering anion radicals are absent, discard this test solution and start with a fresh portion of the original test solution.

6. Add a small amount (~0.2-0.3 g) of NH_4Cl and render the solution ammoniacal with conc. NH_3 solution.

7. Bring to $50-60^\circ\text{C}$ by placing on a hot water bath.

8. Add a concentrated solution (~1M) of $(\text{NH}_4)_2\text{CO}_3$ with stirring. If a precipitate appears, add more $(\text{NH}_4)_2\text{CO}_3$ until precipitation is complete. Keep at $50-60^\circ\text{C}$ for ~3-5 minutes. Filter and wash with little water.

Precipitate

Group -IV

(white)

BaCO_3

SrCO_3

CaCO_3

Filtrate (Group -V)

If Groups (I-IV) are absent, discard the solution and start with a fresh portion of the original test solution.

1. Transfer to a porcelain crucible.
2. Evaporate almost to dryness.
3. Add ~1 ml of conc. HNO_3 and evaporate to dryness in a **FUME CUPBOARD**. Continue heating until the evolution of white fumes of the ammonium salts ceases. Two cases may arise:

No residue is left

Group V absent

A white residue is left.

Group-V present

Take up with
water or dil. HCl

Solution

$(\text{Mg}^{2+}, \text{Na}^+, \text{K}^+)^*$

Confirm by individual tests
(cf. Sect. 4.21-4.23)

* NH_4^+ radical can not be detected here, since ammonium salts and NH_3 have been added to the test solution as reagents.

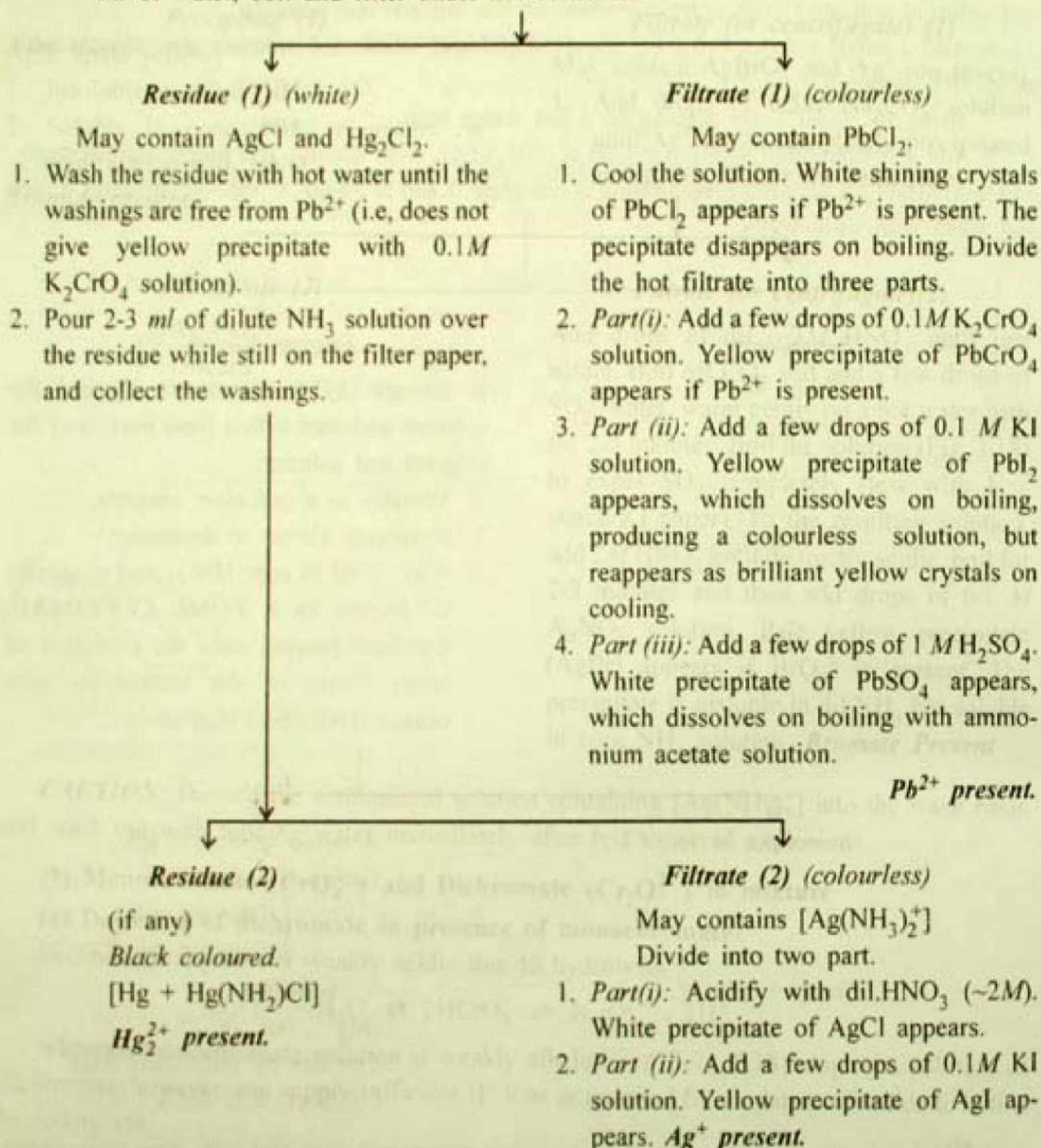
(b) Separation and detection of Group-I cations (Silver Group)

Group-I Precipitate (white)

May contain AgCl , PbCl_2 , Hg_2Cl_2

1. Wash the precipitate on the filter paper first with a little 2M HCl and then with cold water.

2. Transfer the precipitate into a small beaker or to a boiling tube (Fig 3.1c). Add ~5 ml of water, boil and filter under hot condition.



(c) Separation of Group-II sulfides into Group-II(A) and Group-II(B)

Group-II precipitate may contain:

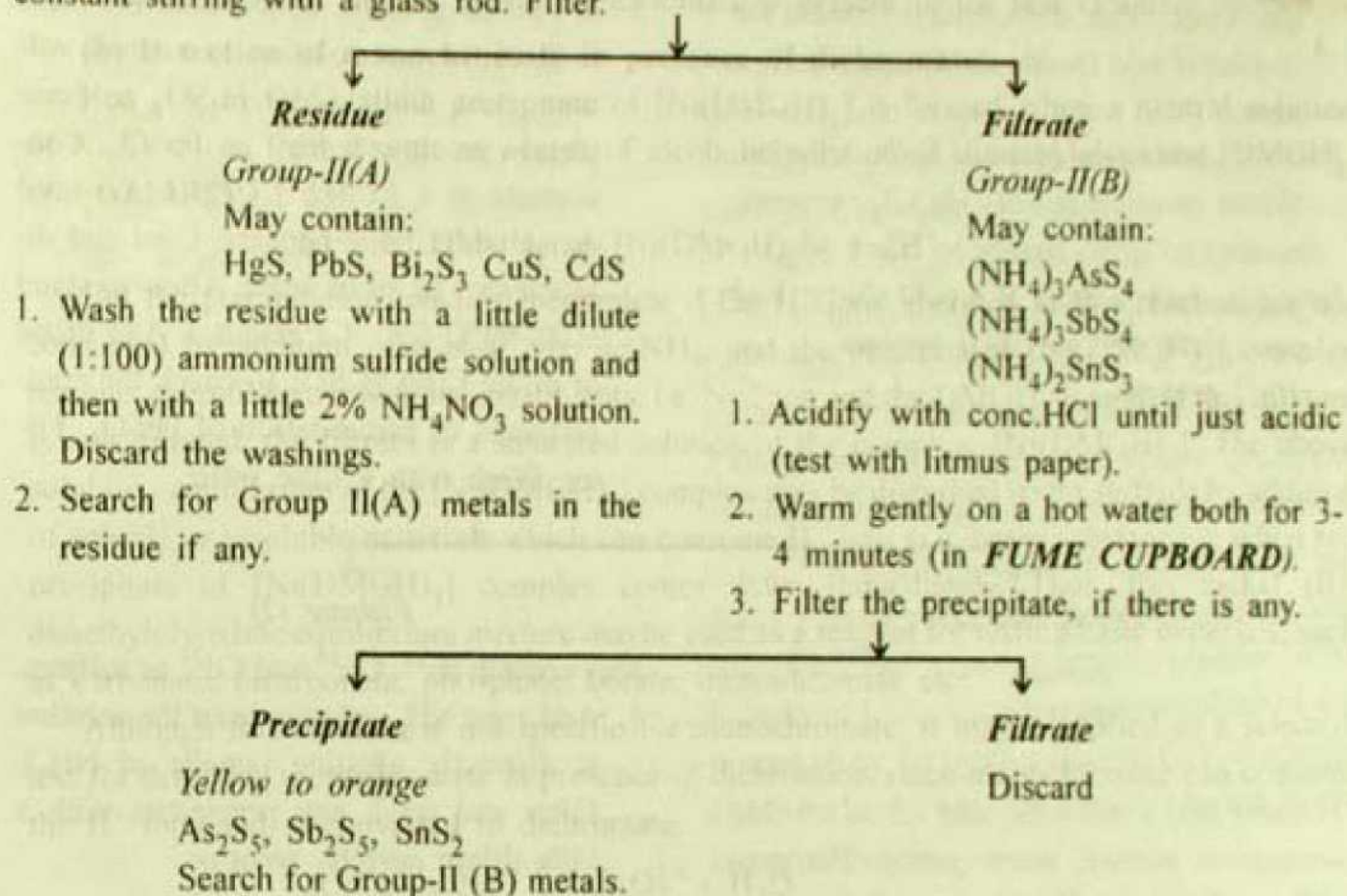
HgS, PbS, Bi₂S₃, CuS, CdS

As₂S₃, Sb₂S₃, SnS, SnS₂

Group-II(A) sulfides.

Group-II(B) sulfides.

Wash the precipitate while still on the filter paper, with a little 5% NH_4Cl solution in H_2S -water (to prevent aerial oxidation of the sulfides to sulfate, CuS to CuSO_4 in particular). Transfer into a small beaker. Add $\sim 5 \text{ ml}$ of yellow ammonium polysulfide, $(\text{NH}_4)_2\text{S}_x$ solution, heat gently to $50\text{-}60^\circ\text{C}$ on a hot water bath in a **FUME CUPBOARD** for $\sim 3\text{-}4$ minutes with constant stirring with a glass rod. Filter.



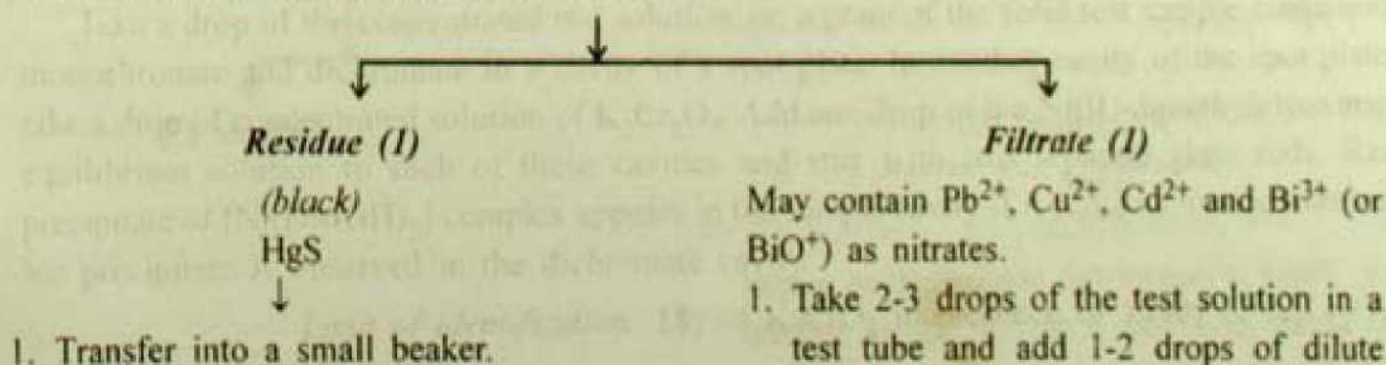
(c)(i) Separation and detection of Group-IIA cations

Group-IIA Precipitate

May contain:

HgS (black)	: CdS (yellow)
PbS (black)	: Bi ₂ S ₃ (brown)
CuS (black)	

1. Transfer the precipitate into a small beaker,
2. Add $4\text{-}5 \text{ ml}$ of dilute (2M) HNO_3 , boil gently for $2\text{-}3$ minutes inside a **FUME CUPBOARD**.
3. Filter and wash with a little water.



Residue (1)

2. Add ~ 1 ml of dil. (2M) HCl and a few drops of NaOCl solution. Boil gently in a **FUME CUPBOARD** to drive off Cl_2 gas. Cool, filter if necessary. Discard the residue if any. Divide the filtrate into two parts:

Part (i) : Add a few drops of SnCl_2 solution. White precipitate of Hg_2Cl_2 appears, turning to grey, finally to black (Hg).

Part (ii): Add 1 drop of Cu_2I_2 slurry. Red precipitate of $\text{Cu}_2[\text{HgI}_4]$ appears.

Hg^{2+} present.

Filtrate (1)

($\sim 2\text{M}$) H_2SO_4 and 2-3 drops of ethanol, mix well. If a heavy white precipitate (PbSO_4) appears, **Pb^{2+} is present.**

2. If Pb^{2+} is present, concentrate the main bulk of the test solution to a small volume. Add dilute (2M) H_2SO_4 to completely precipitate Pb^{2+} as PbSO_4 . Concentrate in a **FUME CUPBOARD** until dense white fume appears. Cool and dilute with ~ 10 ml of water. Allow to stand at $80-90^\circ\text{C}$ for $\sim 4-5$ minutes. Add drops of dilute (2M) H_2SO_4 to check the completeness of precipitation of PbSO_4 . Filter. Wash with a little water.

Precipitate (2)

(white)

PbSO_4



Transfer into a test tube, add ~ 2 ml of 3M ammonium acetate, warm gently. The precipitate dissolves. Divide the solution into two parts and perform the following tests:

Part(i): Add 2-3 drops of dil. (2M) acetic acid and then 1-2 drops of 0.1M K_2CrO_4 solution. Yellow precipitate of PbCrO_4 appears.

Part(ii): Add 1-2 drops of 0.1M KI solution. yellow precipitate of PbI_2 appears. The precipitate dissolves on boiling, reappears as brilliant yellow crystals on cooling **Pb^{2+} present.**

Filtrate (2)

May contain Bi^{3+} , Cu^{2+} and Cd^{2+} as sulfates.

1. Add conc. NH_3 solution until the solution is distinctly alkaline (smells of NH_3). Filter and wash any precipitate with a little dilute aq- NH_3 solution.

Precipitate (3)

white

$\text{Bi}(\text{OH})_3$

1. Place a part of the precipitate on a spot plate and add a few drops of sodium

Filtrate (3)

Precipitate (3)

stannite solution. Black precipitate of metallic Bi appears.

2. Dissolve another part of the precipitate in 2-3 drops of dil. HNO_3 . Place 1 drop of the resulting solution on a drop reaction paper moistened with cinchonine-KI reagent. Orange red spot indicates Bi^{3+} is present.

Filtrate (3)

May contain: $[\text{Cu}(\text{NH}_3)_4]^{2+}$, (deep blue),

$[\text{Cd}(\text{NH}_3)_4]^{2+}$ (colourless).

1. If the colour is deep blue, Cu^{2+} is present.

Place 1-2 drops of this deep blue solution on a spot-plate, add drops of dilute (2M) acetic acid until acidic, then add 1-2 drops of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution. Chocolate or reddish-brown precipitate of $\text{Cu}_2[\text{Fe}(\text{CN})_6]$, confirms Cu^{2+} is present.

2. If the solution is colourless, Cu^{2+} is absent, but Cd^{2+} may be present. Place a drop of the ammoniacal test solution on a spot plate, add 1-2 drops of H_2S - water. If a yellow precipitate of CdS appears, Cd^{2+} is present and confirmed.

3. If Cu^{2+} is present, addition of H_2S -water produces a black precipitate, which definitely contains CuS , but it is not certain whether or not it contains CdS , since the yellow colour of CdS is masked by the black colour of CuS . Under this condition, carry out tests for Cd^{2+} by the following procedures:

- (i) Filter the black precipitate obtained on addition of H_2S -water to the deep blue coloured ammoniacal solution containing the complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion, and wash with a little H_2S -water rendered slightly ammoniacal. Now pass a few drops of dilute HCl (~2M) through the precipitate while still on the filter paper and collect the clear effluent in a test tube. The black precipitate of CuS does not dissolve in dil. HCl solution. To the HCl extract, add a few drops of conc. NH_3 until ammoniacal. If a yellow precipitate (CdS) appears at this stage, Cd^{2+} is present and confirmed.

- (ii) Alternatively, spot a Whatman No. 1 filter paper strip with H_2S -water (or better with freshly precipitated ZnS slurry), allow to dry.

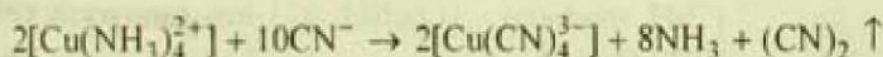
Filtrate (3)

Add a drop of the blue coloured ammoniacal test solution using a capillary tube. Immediate blackening (due to CuS) indicates Cu^{2+} is present. Now hold a solution of dilute (2M) HCl on the spot with the aid of a capillary dropper. A moistened ring starts moving away from the black spot at the center. When the moistened region has moved some distance, (~1 cm) away from the black spot, hold the paper over ammonia vapour. The moistened region is turned yellow coloured (due to CdS) if Cd^{2+} is present.

(iii) Alternatively (**GREAT CAUTION**): Place 1-2 drops of the blue coloured ammoniacal test solution containing the complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ on the spot plate, add drops of 1M KCN solution (from special dropping bottle (Fig. 3.6e) meant for KCN solution) until the blue colour is discharged (as the blue complex $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ion is transformed into colourless complex $[\text{Cu}(\text{CN})_4]^{3-}$ ion. Now add a drop of H_2S - water. A yellow precipitate (of CdS) at this stage *confirms the presence of Cd^{2+}* (cf. Sect 2.3).

(iv) Alternatively, confirm Cd^{2+} by tris-bipyridine iron (II) iodide test. (cf. p. 264).

Note: KCN reacts with both the complexes $[\text{Cu}(\text{NH}_3)_4]^{2+}$ and $[\text{Cd}(\text{NH}_3)_4]^{2+}$ to form the corresponding cyano complexes, $[\text{Cu}(\text{CN})_4]^{3-}$ and $[\text{Cd}(\text{CN})_4]^{2-}$, which are both colourless. Cu^{II} is reduced by CN^- ion to Cu^{I} , which being a softer Lewis acid, forms more stable complex than Cu^{II} with CN^- ion, which is a *soft Lewis base*.



Stability constant of the copper (I) cyano complex, $[\text{Cu}(\text{CN})_4]^{3-}$, is much higher than that of the cadmium (II) cyano complex, $[\text{Cd}(\text{CN})_4]^{2-}$ ion:

	$[\text{Cu}^{\text{I}}(\text{CN})_4]^{3-}$	$[\text{Cd}^{\text{II}}(\text{CN})_4]^{2-}$
$\log \beta_4 (25^\circ\text{C}):$	30.3	17.11

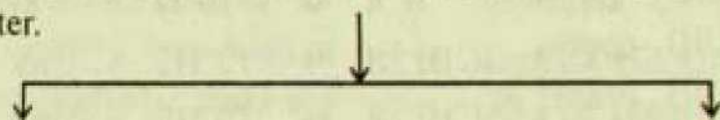
As a result, the concentration of free Cu^{2+} (or Cu^+) ion in presence of excess CN^- ion is much lower than that is required to exceed the solubility product of Cu_2S ($K_{\text{sp}} = 2.5 \times 10^{-48}$ at 25°C) with the sulfide (S^{2-}) ion concentration prevailing in the solution under the condition of the test. Whereas, due to lower stability constant of $[\text{Cd}(\text{CN})_4]^{2-}$ complex,

free Cd^{2+} ion concentration, even in the presence of excess of CN^- ion concentration, is sufficient to exceed the solubility product of CdS ($K_{sp} = 8 \times 10^{-27}$ at 25°C) with the prevailing S^{2-} ion concentration under the condition of the test (*cf.* Sect 2.3 for details).

(c) (ii) Separation and detection of Group-IIB cations

The yellow-orange precipitate of Group-IIB may contain As_2S_5 , As_2S_3 , Sb_2S_5 , SnS_2 , SnS and some S.

1. Wash the precipitate, while still on the filter paper, with a little H_2S -water and discard the washings.
2. Transfer the precipitate into a small conical flask by washing with a jet of water, add $\sim 5 \text{ ml}$ of conc.HCl, put a small funnel on the mouth of the conical flask (Fig. 3.12), boil gently inside a **FUME CUPBOARD** for ~ 5 minutes. Dilute with $\sim 5 \text{ ml}$ of water and allow to stand for 2-3 minutes.
3. Add drops of H_2S -water to reprecipitate small amount of arsenic sulfide which may have dissolved on boiling with conc.HCl. Filter and wash the precipitate (if any) with a little H_2S -water.



Precipitate (1) (yellow)

May contain : As_2S_5 , As_2S_3 and S.

1. Dissolve the precipitate in $\sim 3\text{-}4 \text{ ml}$ of $2M$ NH_3 solution by warming. Filter if necessary. To the filtrate add $3\text{-}4 \text{ ml}$ of 3% H_2O_2 solution and warm gently for 4-5 minutes. H_2O_2 oxidizes As^{III} if any, to As^{V} and sulfide to sulfur. Filter.

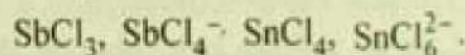
(i) To the filtrate add $2\text{-}3 \text{ ml}$ of $\text{Mg}(\text{NO}_3)_2$ solution (or magnesia mixture). Stirr, add 2-3 drops of $2M$ NH_3 solution if necessary, allow to stand. White crystalline precipitate of $(\text{NH}_4)\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$ appears. **As present.**

(ii) On the filter paper pour $\sim 1 \text{ ml}$ of AgNO_3 solution containing $\sim 0.5 \text{ ml}$ of $1M$ acetic acid. The residue on the filter paper turns brownish-red due to Ag_3AsO_4 .

As present.

Filtrate (1) (colourless)

May contain : Sb^{III} , Sn^{IV} as chloride and chloro complexes:



1. Boil the filtrate inside a **FUME CUPBOARD** to expel H_2S from the solution.
2. Cool and divide the solution into three parts.
3. Search for Sb and Sn by individual tests.

Part (i): Take $\sim 1 \text{ ml}$ of the test solution in a test tube, add drops of $2M$ NH_3 solution until just alkaline (smells NH_3), filter off any slight precipitate at this stage. Add a few crystals of solid oxalic acid and heat to boiling. Add drops of H_2S -water. Orange precipitate of Sb_2S_3 appears. **Sb present.**

Part (ii): Place 1-2 drops of the solution on a spot plate, add a small crystal of sodium nitrite followed by 2 drops of



Filtrate (I) (colourless)

rhodamine-B reagent. Stir with a glass rod. Violet colouration develops.

Sb present.

Part (iii): Take ~1 ml of the solution in a test tube, add drops of 2M NH_3 to partially neutralize the solution (solution should be faintly acidic, test with a litmus paper). Add a few pieces of small clean iron nails (or a small amount of magnesium powder). Warm gently. Sb^{III} , if present, is reduced and precipitated as black metallic Sb on the iron nails. Sn^{IV} is reduced to Sn^{II} -chloride. Filter the solution (*cf.* Fig. 3.21) into a solution of HgCl_2 taken in another test tube. White to grey precipitate containing Hg_2Cl_2 and Hg appears. **Sn present.**

(d) Separation and detection of Group-III A cations

Group-III A Precipitate (Gelatinous)

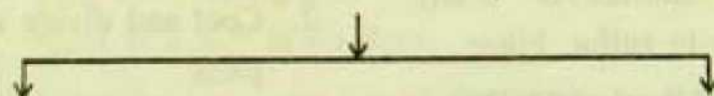
May contain: $\text{Fe}(\text{OH})_3$ (brown)

$\text{Cr}(\text{OH})_3$ (green)

$\text{Al}(\text{OH})_3$ (white) &

$\text{MnO}(\text{OH})_2$ (dirty brown) (may occur in small amount)

1. Wash the precipitate while still on the filter paper with a little 1% NH_4Cl solution containing little NH_3 .
2. Transfer the precipitate into a small beaker (~50 ml), add ~5-10 ml of water and 1-1.5g of sodium peroxoborate, $\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$ (or ~5 ml of dilute 2M NaOH and 5 ml of 6% H_2O_2 solution) to oxidize $\text{Cr}(\text{OH})_3$ to CrO_4^{2-} ion. Boil the mixture gently (for ~3-4 minutes) until the effervescence (due to O_2 evolution) ceases. Filter.



Residue (I)

May contain : $\text{Fe}(\text{OH})_3$ and $\text{MnO}(\text{OH})_2$

1. Wash the precipitate with a little hot water.
2. Take a small amount of the precipitate in a test tube add ~0.5-1 ml of dil. (2M)HCl, warm to get a clear solution, filter/centrifuge if necessary. Take 1-2 drops of the solution on two cavities of a spot plate and perform the following tests:

Filtrate (I)

May contain:

CrO_4^{2-} (yellow)

$\text{Al}(\text{OH})_4^-$ (colourless)

1. If the filtrate is yellow - chromium is present, aluminium may or may not be present.
2. If the filtrate is colourless, chromium is absent, aluminium may or may not be present.

Residue (1)

- (i) Add 1 drop of $0.1M NH_4SCN$ (or $KSCN$) to one cavity, blood red colouration appears due to $Fe(SCN)^{2+}$ ion.

Fe present.

- (ii) Add 1 drop of $K_4[Fe(CN)_6]$ solution to the other cavity, Prussian blue colouration or precipitate appears.

Fe present.

3. Take another portion of the precipitate in a test tube, add 1 ml of $8M HNO_3$ and 3-4 drops of 3% H_2O_2 (or 2-3 drops of SO_2 -water). Boil for a few minutes until decomposition of H_2O_2 (evolution of O_2) ceases or SO_2 is removed from the solution. Add a few grains (~ 0.05 - $0.1g$) of sodium bismuthate, ($NaBiO_3$), shake and allow to settle. Violet colour appears due to MnO_4^- .

Mn present.

Filtrate (1)

3. Perform the following confirmatory tests for chromium (*cf.* Sect. 4.13).

- (i) Place 1-2 drops of the filtrate on a spot plate, add drops of dilute ($2M$) acetic acid until acidic. Add 1 drop of lead acetate solution. Yellow precipitate ($PbCrO_4$) *confirms chromium*.

- (ii) Take $\sim 1 ml$ of the filtrate in a test tube, add drops of dilute ($2M$) HNO_3 until distinctly acidic. Add $\sim 1 ml$ of ether and 3-4 drops of 3% H_2O_2 solution, shake and allow the mixture to stand. Blue upper (organic) layer (due to chromium pentoxide, CrO_5) *confirms chromium*.

4. Perform the following tests for aluminium (*cf.* Sect 4.12).

- (i) Take $\sim 1 ml$ of the filtrate in a semi-micro test tube, add $\sim 0.5g$ of NH_4Cl and boil gently for a few minutes. White gelatinous precipitate of $Al(OH)_3$ appears if aluminium is present. Add a little more NH_4Cl and continue boiling if necessary to obtain a visible precipitate. Centrifuge and wash the precipitate with water, discard the centrifugate until almost neutral (test with litmus paper). To the washed (neutral) precipitate of $Al(OH)_3$ add 1 drop of alizarin-S reagent and place the test tube with its contents in a beaker of boiling water (Fig. 3.15). Beautiful scarlet red lake is formed if aluminium is present. *Al confirmed*.

- (ii) Take $\sim 1 ml$ of the filtrate in a test tube, acidify with dilute ($2M$) HCl , then render alkaline with $aq-NH_3$. White gelatinous precipitate of $Al(OH)_3$ appears. Centrifuge and wash the precipitate with water.

Filtrate (1)

Dissolve the precipitate in ~ 1 ml of 2M HCl, add 1 ml of 6M ammonium acetate and a few drops of aluminon reagent. Add ammonium carbonate until alkaline. Stir with a glass rod. Red precipitate - *Al confirmed*.

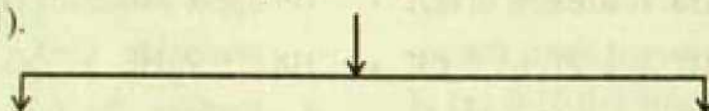
(e) Separation and detection of Group-IIIB cations

Group -IIIB Precipitate

May contain : CoS (black) MnS (flesh coloured)
 NiS (black) ZnS (white)

1. Wash the precipitate, while still on the filter paper, with 1% NH_4Cl solution containing a little NH_3 and a little $(\text{NH}_4)_2\text{S}$ ($\sim 1\%$ by volume), discard the washings.

2. Transfer the precipitate into a small (~ 50 ml) beaker, add ~ 5 ml of dilute (2M) HCl and a little water (~ 5 ml). Stir with a glass rod, allow to stand for 3-4 minutes and filter (cf. Figs. 3.20 or 3.21).



Residue (1) (black)

May contain CoS, NiS.

1. Perform borax bead test with the residue.

- (i) Blue bead in both oxidizing and reducing flame - *Co present and confirmed*.
- (ii) Brown bead in oxidizing flame and grey bead in reducing flame - *Ni present*.

2. Transfer the precipitate into a small (~ 25 ml) beaker, add 1-2 ml of sodium hypochlorite (NaOCl) solution and ~ 1 ml of dilute (2M) HCl. Boil the mixture gently until evolution of Cl_2 gas ceases. Cool the solution and search for Co(II) and Ni(II) by the following individual tests. (cf. Sects. 4.14, 4.15)

- (i) Take ~ 1 ml of the solution in a test tube, add 1 ml of ether and 1-2 small crystals of KSCN, or, NH_4SCN , shake. Blue colouration of the organic layer.

Co present and confirmed.

- (ii) Take 1 ml of the solution and 1 ml of

Filtrate (1) (colourless)

May contain Mn^{2+} , Zn^{2+} , (if coloured, traces of Co^{2+} , Ni^{2+} may occur).

- 1. Boil gently to remove the H_2S gas completely (test with lead acetate paper).
- 2. Cool the solution and add 2M NaOH solution in excess until strongly alkaline. Add ~ 1 ml of 3% H_2O_2 solution, boil gently for 3-4 minutes (to oxidize Mn^{II} to Mn^{IV}). When effervescence (O_2 evolution) ceases, filter.



(Continued p. 513)

Residue (1) (black)

conc. HCl in a test tube, warm gently, deep green colour (due to CoCl_4^{2-}) develops. Cool and dilute with water, the green colour disappears, a redish pink colour (due to $\text{Co}^{2+}(\text{aq})$) appears. **Co present and confirmed.**

(iii) Place 1-2 drops of the solution on a spot plate, add 1 drop of 1% alcoholic dimethylglyoxime reagent and drops of dilute aq-NH_3 until ammoniacal. Crystalline red precipitate appears. **Ni present and confirmed.**

Filtrate (1) (colourless)

Precipitate (2)

$\text{MnO}(\text{OH})_2$ (dirty brown)

(traces of $\text{Co}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$ may occur) Dissolve the precipitate in $\sim 5 \text{ ml}$ of $8M \text{ HNO}_3$, adding a few drops of $3\% \text{ H}_2\text{O}_2$ (to reduce Mn^{IV} to Mn^{II}). Boil gently until effervescence ($\text{O}_2 \uparrow$) ceases. Divide the solution into three parts and perform the following tests (cf. Sect 4.16).

Part (i): Place 1-2 drops of the solution on a spot plate and add a few grains of sodium bismuthate (NaBiO_3). Stir with a glass rod. Violet colouration (due to MnO_4^-). **Mn present and confirmed.**

Part (ii): Take $\sim 1 \text{ ml}$ of the solution in a test tube, add 1 drop of AgNO_3 solution and a crystal of potassium (or ammonium) peroxodisulfate ($\text{K}_2\text{S}_2\text{O}_8$). Warm gently. Violet colour due to MnO_4^- develops. **Mn present and confirmed.**

Part (iii): Take 1 ml of the solution, add a small amount of red lead (Pb_3O_4) in a test tube and boil gently. Violet colour due to MnO_4^- ion develops. **Mn present and confirmed.**

Filtrate (2) (colourless)

May contain $\text{Zn}(\text{OH})_4^{2-}$. Acidify with acetic acid ($2M$), divide into three parts and perform the following tests (cf. Sect 4.17).

Part (i): Take 1 ml of the solution in a test tube add H_2S - water. White precipitate of ZnS appears.

Zn-present.

Part (ii): Place 1 drop of the solution on a spot plate, add 1 drop of very dilute copper sulfate solution and then 1 drop of ammonium mercuriothiocyanate solution. Stir with a glass rod. Violet precipitate appears.

Zn present and confirmed.

Part (iii): Perform the above test (ii) using 1 drop of cobalt nitrate solution in place of copper sulfate. A blue precipitate appears.

Zn present and confirmed.

(f) Separation and detection of Group-IV cations

Group-IV Precipitate (white)

May contain : BaCO_3 , SrCO_3 and CaCO_3

1. Wash the precipitate, while still on the filter paper, with a little hot water, discard the washings.
2. Pour drops of hot dilute (2M) acetic acid through the filter paper repeatedly and collect the effluent (~2ml). Heat nearly to boiling. Call this solution as (*solution-A*)
3. Place 1-2 drops of the hot acetic acid extract (i.e. *solution A*) on a spot plate, add 1-2 drops of 0.1 M, K_2CrO_4 solution. Yellow precipitate (BaCrO_4) indicates and **confirms the presence of Ba**.
4. If Ba is absent, discard the portion used in testing for Ba. Search for Sr^{2+} and Ca^{2+} in remainder of *solution-A*.
5. If barium is present, add sufficient 0.1 M K_2CrO_4 to the remainder of *solution - A* to precipitate BaCrO_4 completely. Heat nearly to boiling and allow to stand. Add a few more drops of the K_2CrO_4 solution to ensure that precipitation of BaCrO_4 is complete and the supernatant liquid is yellow coloured. Filter and wash the precipitate with hot water. Search for Sr^{2+} and Ca^{2+} in the combined filtrate and washings.



Precipitate (1)

BaCrO_4 (yellow)

1. Take a small portion of the precipitate in a porcelain dish, add 2-3 drops of conc.HCl. Evaporate the resulting solution inside a **FUME CUPBOARD** almost to dryness.
2. Carry out flame test with the residue. Apple green (yellowish-green) flame.
Ba present and confirmed.

(Filtrate + washings) (1) - yellow

May contain Sr^{2+} and Ca^{2+}

1. To the hot filtrate, add 2M ammonia solution until ammoniacal (smells NH_3).
2. Add a saturated solution of $(\text{NH}_4)_2\text{CO}_3$ (or Na_2CO_3) in excess. White precipitates of SrCO_3 and or CaCO_3 appear.
3. Filter and wash the precipitate with hot water, while still on the filter paper.
4. Pour drops of hot 2M acetic acid solution on the precipitate on the filter paper and collect the effluent. Call this solution as (*solution-B*)

Both (*solution-A* if Ba^{2+} is absent) and (*solution-B* if Ba^{2+} is present) may contain Sr^{2+} and Ca^{2+} . Proceed according to the following procedure.

Solution-A or Solution-B (as the case may be).

1. Boil gently to expel CO_2 completely. Concentrate the volume nearly to ~5 ml.
2. Take ~2 ml of the test solution in a test tube, add ~2 ml of saturated $(\text{NH}_4)_2\text{SO}_4$ solution

and a small crystal of sodium thiosulfate (or ~2 ml of triethanolamine), warm the mixture gently on a hot water bath with constant stirring with a glass rod for 5 minutes. Allow to stand for 2-3 minutes and filter.

Precipitate (2) (white)
SrSO₄ mostly.

Filtrate (2) (colourless)
May contain Ca²⁺

1. Place the filter paper containing the precipitate in a porcelain or silica crucible. Heat strongly until the filter paper is charred. Alternatively, hold the filter paper with the precipitate at the Bunsen flame with the aid of a Pt-wire.
2. Moisten the resulting ash with conc.HCl and perform flame test. Crimson red flame *indicates and confirms* Sr²⁺.

(If Sr²⁺ is absent use *solution-A* or *solution-B* directly for testing Ca²⁺).

To 2 ml of the test solution in a test tube, add 2 ml of saturated ammonium oxalate, (NH₄)₂C₂O₄ solution and drops of aq-NH₃ until almost neutral. Warm on a hot water bath (Fig. 3.15). White precipitate (CaC₂O₄) indicates *Ca present*.

Confirm Ca by flame test. Transient brick-red flame *confirms* Ca²⁺.

(g) Separation and detection of Group-V cations

Note: If the metals of Groups I to IV are absent, search for Group-V cations in the original test solution. Otherwise, search for Group-V cations in the filtrate obtained after precipitation of Group-IV metal carbonates. In either case, evaporate the solution to dryness. Moisten the resulting residue with a few drops of conc.HNO₃ and heat inside a **FUME CUPBOARD** to decompose and drive off ammonium salts. Cool and extract the residue, if any, with minimum volume of water, filter if necessary.

Residue (1) (if any)

Filtrate (1) (colourless)

1. Dissolve in a few drops of hot 2M HCl, dilute with equal volume of water. Divide the solution into three parts and test for Mg²⁺ (cf. Sect. 4.21).

Part (i): To 2-3 drops of the test solution on a spot plate, add 2 drops of magneson reagent and drops of 2M NaOH solution until alkaline. Blue precipitate.

Mg-present and confirmed.

Part (ii): Place a drop of the test solution on a spot plate, add a drop of titan yellow reagent and drops of 2M NaOH until

Concentrate into a small volume, divide into four parts and test for Mg²⁺, Na⁺ and K⁺ (cf. Sect. 4.21-4.23).

Part (i): Place 1-2 drops of the test solution on a spot plate, add 1 drop of oxine reagent and drops of dilute aq-NH₃ (~2M) until faintly ammoniacal. Pale yellow precipitate: *Mg present*.

Part (ii): Take ~1 drop of the test solution in a test tube, add 1 drop of Na₂HPO₄ solution and drops 2M ammonia solution until ammoniacal. Warm on a hot water

Residue (I) (if any)

alkaline. Red colouration or a precipitate indicates **Mg-present and confirmed**.

Part (iii): Take ~0.5 ml of the test solution in a test tube, add a few small crystals of NH_4Cl and warm. To the hot solution add 1 drop of oxine reagent and drops of 2M aq- NH_3 until faintly alkaline. Pale yellow precipitate. **Mg present.**

Filtrate (I) (colourless)

bath, scratch the sides of the test tube with a glass rod. White crystalline precipitate ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) appears.

Mg-present.

Part (iii): To 1 drop of the test solution on a spot plate, add 8 drops of zincuranylacetate reagent, stir with a glass rod. Yellow crystalline precipitate appears within a short time. **Na present.** Confirm by flame test.

Part (iv): Take 1-2 drops of the test solution on a spot plate, add a few drops of sodium cobaltinitrite ($\text{Na}_3[\text{Co}(\text{NO}_2)_6]$) in 2M acetic acid, stir with a glass rod. Yellow precipitate of $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ appears within a short time. **K present.** Confirm by flame test.

7.9 Testing of Insoluble Residues

Colour of majority of the common insoluble materials are white, a limited number of insoluble materials have characteristic colours.

(1) Colours of common insoluble materials

Insoluble Residue (D)

Characteristic colour

Green Cr_2O_3

Red Fe_2O_3

Yellow PbCrO_4

Pale yellow AgX ($\text{X} = \text{Br}, \text{I}, \text{SCN}$)[#]

Grey CaF_2

White coloured

$\text{PbSO}_4, \text{BaSO}_4, \text{SrSO}_4, \text{CaSO}_4$

$\text{Al}_2\text{O}_3, \text{SiO}_2, \text{SnO}_2, \text{AgCl}$ [#]

(Ca, Mg, Al) silicates.

Compounds of rare elements

$[\text{BeO}, \text{CeO}_2, \text{TiO}_2, \text{ZrO}_2]$ ^{*}

Note:

(i) Acid insoluble sulfides, viz, $\text{As}_2\text{S}_3, \text{As}_2\text{S}_5, \text{Sb}_2\text{S}_3, \text{Sb}_2\text{S}_5, \text{SnS}_2$ (also $\text{MoS}_3, \text{V}_2\text{S}_5$ and WS_3)^{*} dissolve in NaOH, or, KOH solution forming sulfosalts.

(ii) Acidic oxides $[\text{MoO}_3, \text{WO}_3, \text{V}_2\text{O}_5]$ ^{*} are acid insoluble, but dissolves in aq- NH_3 solution forming ammonium salts of the corresponding metalloacids.

(iii) CdS, HgS may be decomposed by fusion with NaOH.

(iv) PbCrO_4 dissolves on boiling with conc. NaOH solution (cf. p. 593).

^{*}Rare elements. [#] May appear slightly ash coloured.

(2) Treatment of insoluble materials

(a) Search for PbSO_4 (white insoluble residue)

Take a small amount ($<0.1\text{g}$) of the insoluble residue in a semi-micro test tube, add $\sim 2\text{ ml}$ of concentrated ($6M$) ammonium acetate solution and a few drops of ammonia, boil gently for 2-3 minutes. If the precipitate dissolves completely, search for only PbSO_4 . Divide the solution into three parts and perform the following test (*cf.* Sect 4.4)

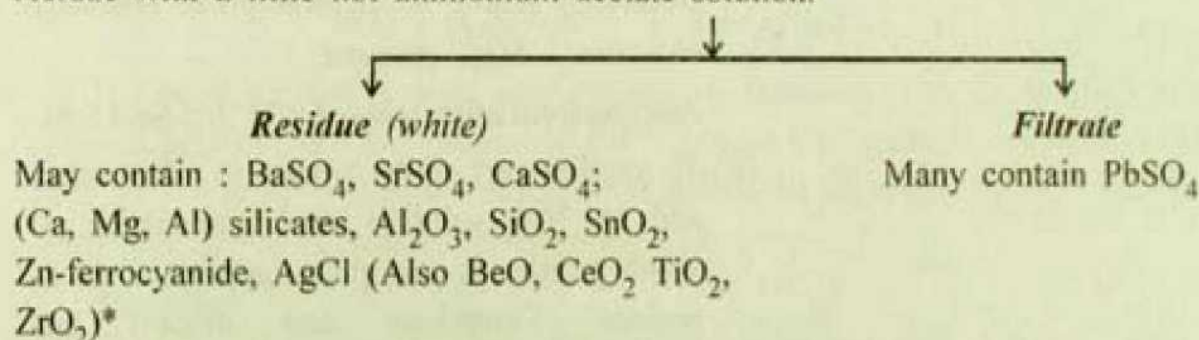
Part (i): Place 1-2 drops of the test solution on a spot plate and add 1 drop of $0.1M$ K_2CrO_4 solution. Yellow precipitate of PbCrO_4 appears. ***Pb present.***

Part (ii): Place 1-2 drops of the test solution on a spot plate and add 1 drop of $0.1M$ KI solution. Yellow crystalline precipitate of PbI_2 appears. ***Pb present.***

Part (iii): Take $\sim 1\text{ ml}$ of the test solution in a semi-micro test tube, acidify with dilute ($2M$) HNO_3 and add drops of $\text{Ba}(\text{NO}_3)_2$ solution. Heavy white precipitate of BaSO_4 appears. ***SO_4^{2-} present and confirmed.***

As the ammonium acetate extract contains both Pb^{2+} and SO_4^{2-} , therefore, ***PbSO_4 is present and confirmed.***

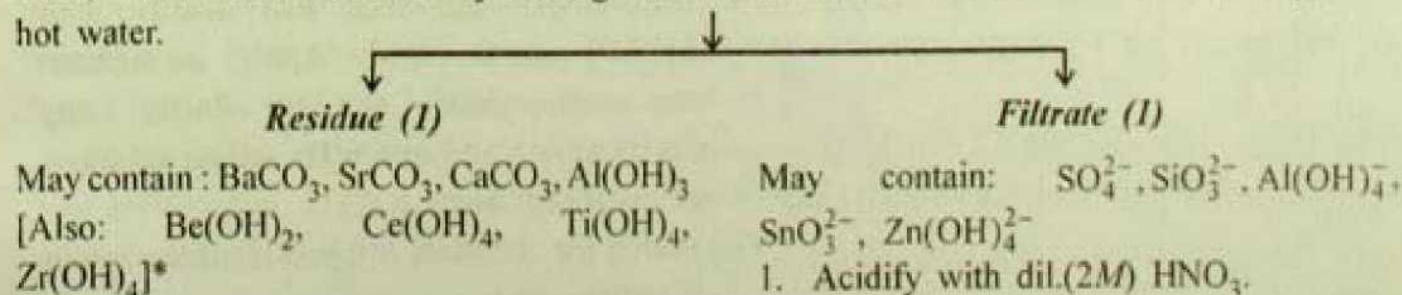
If PbSO_4 is present, boil the remainder of the remainder of the insoluble residue with $6M$ ammonium acetate, until PbSO_4 dissolves completely. Filter under hot condition and wash the residue with a little hot ammonium acetate solution.



If PbSO_4 is absent, proceed to carbonate fusion/bisulfate fusion with the original white insoluble residue.

(b) Carbonate Fusion for white (as well as coloured) insoluble residues

Transfer the insoluble residue into a Nickel or a Platinum crucible. Evaporate to dryness. Mix with 4-times its bulk of fusion mixture (1:1 mixture of anhydrous Na_2CO_3 and K_2CO_3). Heat the mixture strongly until a clear melt results. Keep under molten condition for ~ 5 minutes. Cool, extract the fused mass by boiling with water. Filter and wash the residue (if any) with hot water.



*Rare elements

Residue (1)

1. Extract with dilute (2M) HNO_3 .
2. Search for cations by individual tests, particularly for Group-IIIA, IV and V (Mg). (cf. Sects. 4.12, 4.18-4.20, 7.8d, 7.8.f, 7.8.g and [8.2-8.6]*)

Filtrate (1)

2. Perform individual tests.
Divide into three parts and perform the following tests.
- Part (i):** Perform silico molybdate-benzidine blue test for silicate (cf. Sect. 5.21)
- Part (ii):** Add H_2S - water and then acidify with dil.(2M) HCl . Yellow precipitate (SnS_2). **SnO_2 Present.**
- Part (iii):** Acidify with dilute (2M) HNO_3 , filter or centrifuge if any precipitate appears at this stage.



Precipitate (2) (if any)

- (i) Test for SiO_3^{2-} (SiO_2) (cf. Sect. 5.21)
- (ii) Test for SnO_2 (cf. Sect 4.10)

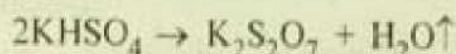
Filtrate (2)

- (i) Test for SO_4^{2-} .
Add $\text{Ba}(\text{NO}_3)_2$ solution to one part of the filtrate. A heavy white precipitate (BaSO_4) indicates - **SO_4^{2-} present.**
Also perform other tests of SO_4^{2-} (cf. Sect 5.9).
- (ii) To another part of the filtrate in a test tube, add 2M NH_3 solution until ammoniacal. A white gelatinous precipitate appears if Al is present. Centrifuge and discard the centrifugate. Wash the precipitate with water by repeated centrifugation until free from alkali. Add 1 drop of alizarin-S reagent and place the test tube in a beaker of boiling water (cf. Fig 3.15). Scarlet red lake indicates-Al. **Al_2O_3 present.**
- (iii) Neutralize ~1 ml of the test solution with dil.(2M) NH_3 and then just acidify with dil.(2M) acetic acid. Apply ammonium mercuriothiocyanate test for Zn(II) using Co(II) nitrate and or Cu(II) sulfate solutions as usual (cf. Sect. 4.17).
- (iv) Search for chromate (cf. p.-425) if the colour is yellow-orange.

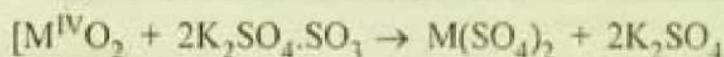
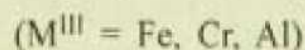
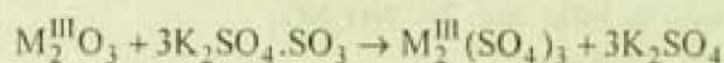
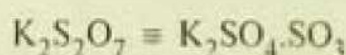
*Rare elements

(c) Bisulfate fusion (for white as well as coloured insoluble residues)

When strongly heated, potassium hydrogensulfate, KHSO_4 , is dehydrated to potassium pyrosulfate, $\text{K}_2\text{S}_2\text{O}_7$:



The pyrosulfate melt acts as a high temperature *Lewis acid* that dissolves the refractory oxides viz. Cr_2O_3 , Fe_2O_3 , Al_2O_3 [and also BeO , CeO_2 , TiO_2 , ZrO_2]* etc. which act as *Lewis bases*. These are transformed to water soluble sulfate salts of the corresponding metals. Pyrosulfate ($\text{S}_2\text{O}_7^{2-}$) ion may be regarded as a (1:1) combination of SO_4^{2-} ion and SO_3 , of which the latter serves as the actual acid.



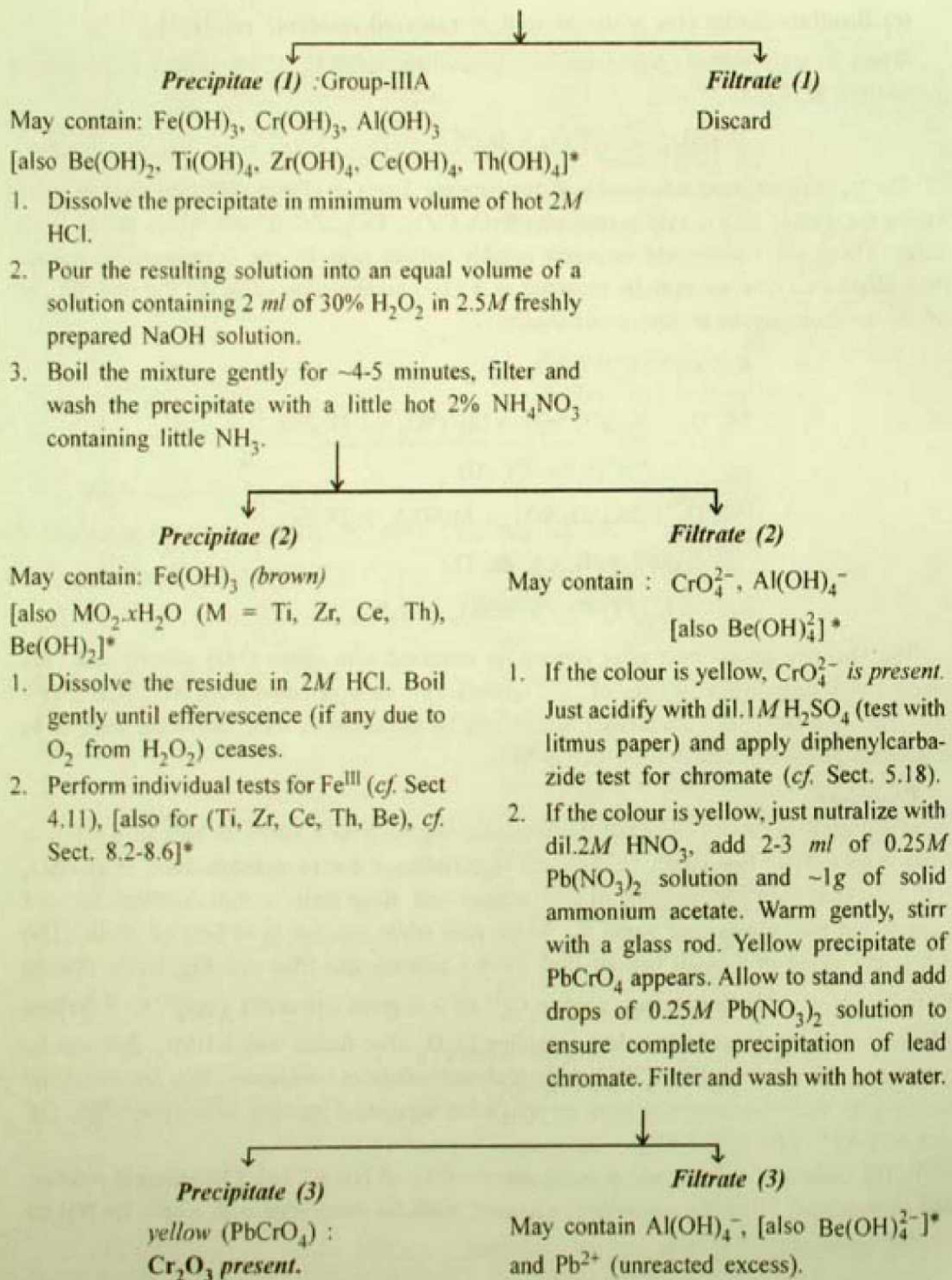
The bisulfate fusion melt after cooling, is extracted with dilute (1M) sulfuric acid. The solution may contain the sulfates of Cr^{3+} (green), Fe^{3+} (almost colourless), Al^{III} , $[\text{Ce}^{\text{III}}, \text{Ti}^{\text{IV}}, \text{Zr}^{\text{IV}}, \text{Th}^{\text{IV}} \text{ and } \text{Be}^{\text{II}}]^*$ (all colourless), which may be identified by their individual tests, or by systematic group separation from Group-III A.

Procedure

Mix a small amount (~0.2g) of the insoluble residue with 4 times its bulk of KHSO_4 in a fusion tube. Heat first gently to drive off H_2O (released due to transformation of 2KHSO_4 to $\text{K}_2\text{S}_2\text{O}_7$) and then very strongly to form a clear melt. Keep under molten condition for ~3-4 minutes and then plunge and break the fusion tube while still hot in ~15-20 ml of dil. (1M) H_2SO_4 contained in a small beaker. Boil for 4-5 minutes and filter (cf. Fig. 3.21). Discard the residue if any. The filtrate may contain Cr^{3+} (if it is green coloured), CrO_4^{2-} , Ce^{IV} (yellow coloured). The other insoluble oxides including Fe_2O_3 after fusion with KHSO_4 , followed by extraction with dilute (1M) H_2SO_4 produce almost colourless solutions. Test for individual members by their characteristic tests, or by Group separation starting from Group-III A. [cf. Sect 4.11-4.13, 7.84, (8.2-8.6)*].

To the clear, hot extract, add a small amount ~0.5g of NH_4Cl and 2M ammonia solution until ammoniacal. Filter if a precipitate is formed, wash the precipitate with a little 1% NH_4Cl solution containing little NH_3 .

*Rare elements



*Rare elements

Filtrate (3)

1. Add drops of H_2S -water until Pb^{2+} is completely precipitated as PbS (black precipitate). Filter and discard the precipitate.
2. Add drops of $2M HNO_3$ until distinctly acidic. Boil off H_2S completely.
3. Add drops of $2M aq-NH_3$ to the hot solution until it is neutral. Add an excess of concentrated $(NH_4)_2CO_3$ solution.
White gelatinous precipitate appears if Al^{3+} is present. Filter (or, centrifuge)

Precipitate (4)

Gelatinous white, $Al(OH)_3$.
Confirm Al by alizarin-S test (cf. Sect. 4.12)

Filtrate (4)

[May contain $[Be(CO_3)_2]^{2-}$ complex ion.

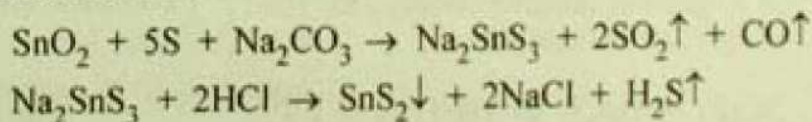
1. Boil gently for some time. White precipitate of $Be(OH)_2$ appears if Be is present.
2. Centrifuge, wash with a little water.
3. Confirm Be by quinalizarin test (cf. Sect 8.2)]*

(d) Tests for SnO_2

(i) Sulfur fusion test

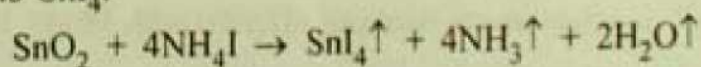
Mix a small amount ($<0.1g$) of the insoluble residue with 4 times of its bulk of (3:2) sulfur powder and fusion mixture in a fusion tube. Heat strongly inside a **FUME CUPBOARD** until fusion occurs. Extract the fused mass with a little hot water, filter and acidify the filtrate with $dil.(2M)HCl$. Yellow precipitate of SnS_2 appears. **SnO_2 is present.**

The probable reactions are :



(ii) Volatilization test

Mix a small amount of the insoluble residue with 4 times its bulk of ammonium iodide (NH_4I) in a porcelain basin and heat the mixture strongly inside a **FUME CUPBOARD**. The sample volatilizes as SnI_4 .



Repeat the operation. If the sample is completely volatilized, **SnO_2 is present.**

*Rare element

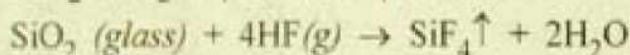
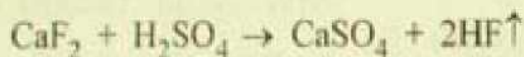
(iii) Luminescence reaction

Take a small amount (<0.1 g) of the insoluble residue in a small beaker (25-50 ml) and cover the solid with 5-6 ml of conc.HCl. Add few small pieces of Zn-ganules to liberate H₂ gas. Stirr the mixture with a small test tube filled with cold water. Remove the test tube from the liquid and hold the portion that was immersed in the liquid to the non-luminons Bunsen flame.

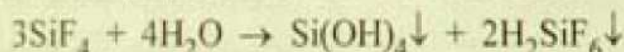
A characteristic blue mantle of the flame is formed around the test tube, even in presence of trace quantities of tin. *SnO₂ is present.*

(e) Tests for CaF₂

(1) Take a small amount (<0.1 g) of the insoluble residue in a dry test tube, add 0.5-1 ml of conc.H₂SO₄ and warm gently inside a **FUME CUPBOARD**. Oily bubbles appear inside the test tube (cf. Sect 5.10)



Hold a drop of water contained in a platinum wire loop over the issuing gas (SiF₄ mostly). The water drop becomes opaque, because of the reaction:



$\therefore$ Fluoride is present.

(2) Continue digestion of the insoluble residue with conc.H₂SO₄ (test 1) inside a **FUME CUPBOARD** for ~5 minutes to dissolve the insoluble residue as much as possible. Cool and pour this reaction mixture in a beaker containing 5-10 ml of water. Filter Add a small amount of NH₄Cl and 2M aq-NH₃ to the filtrate until alkaline. Add drops of concentrated solution of (NH₄)₂CO₃. White precipitate of CaCO₃ appears if CaF₂ is present. Confirm hy flame test. Transient brick red flame confirms calcium. *Ca is present* (cf. Sect 6.5).

(3) Take a small amount (<0.1 g) of the insoluble residue in a test tube add drops of beryllium chloride or nitrate solution, warm gently. The insoluble fluoride residue passes into the solution completely due to the formation tetrafluoroberyllate [BeF₄²⁻] complex ion. Filter/centrifuge if necessary.



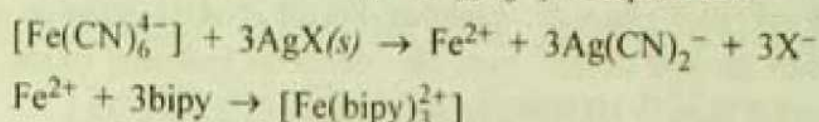
To the clear centrifugate add drops of 2M NH₃ until alkaline and then drops of concentrated (~6M) solution of (NH₄)₂CO₃. White precipitate of CaCO₃ appears if Ca is present. Filter/centrifuge, discard the solution. Perform flame test with the precipitate. Transient brick red flame *confirms Ca*.

Note: The smaller Be²⁺ ion has much stronger affinity than larger size Ca²⁺ ion for the small hard F⁻ ion.

(f) Test for Silver Halides/Pseudohalides: AgX (X = Cl, Br, I, SCN)

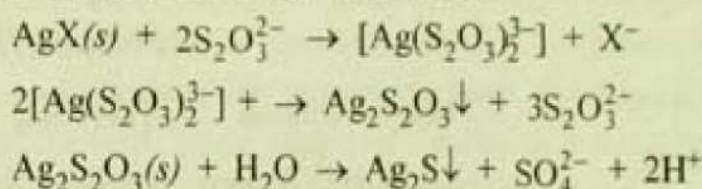
(1) When Silver halides react with warm ammoniacal solution of K₄[Fe(CN)₆] containing

2,2'-bipyridine (bipy), Fe^{2+} is demasked from the cyanocomplex and reacts with bipy, producing a red colouration due to the formation of $[\text{Fe}(\text{bipy})_3]^{2+}$ complex ion:



Take a little (<0.1 g) of the insoluble residue in a semi-micro test tube, add 1-2 drops of 1% $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution followed by 1-2 drops of 2M aq- NH_3 and 1 drop of 1% solution of 2, 2'-bipyridine in alcohol. Place the mixture on a hot water bath (Fig. 3.15) for a few minutes. Depending upon the quantity and also on the nature of the silver halide/pseudo halide ($\text{Cl}^-/\text{Br}^-/\text{I}^-/\text{SCN}^-$), the initially colourless solution gradually becomes pink and finally deep red within a few minutes. (cf. Sect. 5.11).

(2) Silver halides (AgX , $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) dissolve in sodium thiosulfate solution due to the formation of soluble dithiosulfatoargentate(I) complex, $[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}$ ion. The solution on boiling gives black precipitate of silver sulfide.



(3) Silver halides are reduced to silver metal by metallic zinc in presence of dil. H_2SO_4 and halide ions are set free in solution.

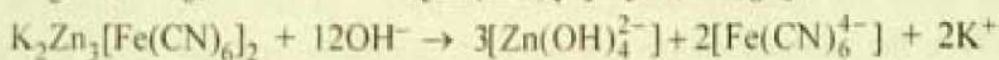
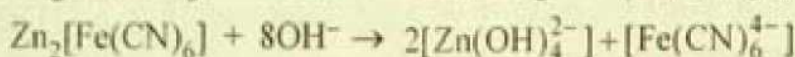
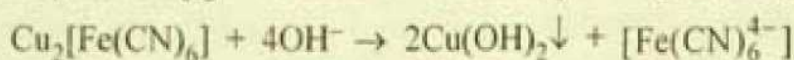
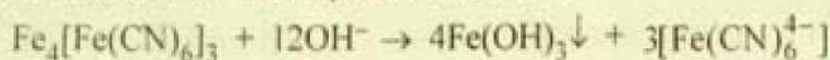
Take a small amount of the insoluble residue in a small (25-50 ml) beaker, add ~5 ml of dil.1M H_2SO_4 and a small amount of zinc-dust. Stirr with a glass rod for ~5-10 minutes. Filter and wash the residue with a little water.

↓	↓	↓
<i>Residue</i>		<i>Filtrate</i>
Spongy mass ($\text{Ag}^0 + \text{Zn}^0$)		May contain $\text{Zn}^{II}\text{Cl}_2$, ZnBr_2 , ZnI_2 , $\text{Zn}(\text{SCN})_2$. Search for halide/ SCN^- ions by individual tests. (cf. Sects. 5.6, 5.11-5.13)
Dissolve the mass in dil.(2M) HNO_3 and to the resulting solution add dil.(2M) HCl .		
Curdy white precipitate of AgCl appears.		
The precipitate dissolves in dil.(2M) NH_3 solution, but reappears on acidification with dil. HNO_3 . <i>Ag-present and confirmed.</i>		

(g) Insoluble ferrocyanides

$\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$	<i>Prussian blue</i>
$\text{Cu}_2[\text{Fe}(\text{CN})_6]$	<i>Chocolate colour</i>
$\text{Zn}_2[\text{Fe}(\text{CN})_6]$	<i>Pale yellow</i>
$\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$	<i>Pale yellow.</i>

In soluble ferrocyanides are decomposed by prolonged treatment with conc. 5M NaOH solution under hot condition. Fe^{III} , Cu^{II} precipitate as their hydrated oxides. Zn^{II} , because of amphoteric nature of its hydroxide, remains in the NaOH solution as sodium zincate, $\text{Na}_2[\text{Zn}(\text{OH})_4]$. Small amount of Zn^{II} may also occur as hydrated oxide, in the residue, like hydrated $\text{Cu}(\text{II})$ -oxide due to incomplete conversion:



Procedure

Take a small amount (~0.1 g) of the insoluble residue in a small beaker, add ~4-5 ml of 5M NaOH solution warm gently, cool and filter.

Residue (I)

$\text{Cu}(\text{OH})_2/\text{CuO}$, $\text{Fe}(\text{OH})_3/\text{FeO}(\text{OH})$, also $\text{Zn}(\text{OH})_2$ (small amount).

Dissolve the residue in hot dilute 2M HNO_3 . Divide into two parts.

Part (i): Take 1 drops of the test solution on a spot plate, add 1 drop of NH_4SCN solution. If a blood red colouration appears, **Fe is present**.

Part (ii): Take ~0.5-1 ml of the test solution, add 2M aq-ammonia solution. If a deep blue colouration appears, **Cu is present**.

Apply other tests of Fe (cf. Sect 4.11). and Cu (cf. Sect. 4.6).

Filtrate (I)

May contain : $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Zn}(\text{OH})_4]^{2-}$ ions. Confirm by individual tests. (cf. Sect. 5.16, 5.17 and 4.17).

Divide into three parts and perform the following tests:

Part (i): Place 1 drop of the test solution on a spot plate, acidify with drops of dil.4M H_2SO_4 and add 1 drop of FeSO_4 or Mohr's salt solution. If a blue colouration or precipitate appears **Ferricyanide is present**.

Part (ii): Place 1 drop of the test solution on a spot plate, acidify with dil.(1:1) HCl solution and add 1 drop of FeCl_3 solution. If a blue colouration or precipitate appears, **Ferrocyanide is present**.

Part (iii): Take ~ 1 ml of the test solution, add dil.2M acetic acid until faintly acidic. Add H_2S -water. If a white precipitate (ZnS) appears, **Zn is present**.

Filter, or, centrifuge, wash with a little water. dissolve the precipitate in dil.2M NaOH solution, acidify with dil.2M acetic acid, apply ammonium mercuriothiocyanate test for zinc using cobalt nitrate or copper sulfate solution as usual (cf. Sect. 4.17).



CHAPTER - 8

Reactions of Cation and Anion Radicals Derived from some 'Rare Elements'

8.1 Introduction

The importance of studying the chemical reactions of the cation and or anion radicals derived from some less common elements, popularly called as *rare elements* and designing experiments for their detection and identification in some natural, industrial, domestic and environmental materials owe their origin in the identification of some of these elements viz, vanadium and molybdenum in several redox enzymes, applications of thorium and uranium in nuclear reactors, beryllium, titanium, zirconium, cerium oxides in producing refractory and high temperature materials, use of titanium, vanadium, tungsten in making special alloys including alloy steels, catalytic properties of certain simple and organometallic compounds of molybdenum, vanadium, and titanium, last but not the least, toxicity of compounds of most of these elements. Although the term, 'rare elements' indicates low natural abundance, which is true for some of these elements, but the term is a misnomer for the other elements so called, and more over, the natural abundances of some common elements, not given the tag of rare elements, are even lower than those of some of the so called rare elements. This will be evident from the weight percent (w%) of the so called rare elements and some common elements (Table 8.1).

Table 8.1. Weight percent (w%) of some less common and common elements in the in the earth crust.

<i>Less common elements (w%)</i>				<i>Common elements (w%)</i>			
Be	6×10^{-4}	V	0.015	Zn	0.013	Cr	0.02
Ti	0.44	Mo	$10^{-3} - 10^{-4}$	Cd	1.5×10^{-5}	Fe	5
Zr	0.022	W	$10^{-3} - 10^{-4}$	Hg	$10^{-5} - 10^{-6}$	Co	2.3×10^{-3}
Hf	4.5×10^{-4}					Ni	8×10^{-3}

Several anomalies may be pointed out from the above table:

(i) Although Cr, Co and Ni are much less abundant than Ti, and Zr, Co and Ni are less abundant than vanadium, yet these elements (Cr, Co and Ni) are not included in the list of rare elements.

(ii) Abundance of Zn is lower than those of Ti, V and Zr, but Zn is not tagged as a rare element, whereas, Ti, V and Zr are called rare elements

(iii) Cd and Hg are much less abundant than almost all the so called rare elements, but yet these are included as common elements.

This chapter deals with the identifying tests of some of these less common elements, viz., beryllium (Be), titanium (Ti), zirconium (Zr), vanadium (V), molybdenum (Mo), tungsten (W),

cerium (Ce), thorium (Th) and uranium (U), when they are present singly as well as in their binary and ternary mixtures. Although these elements may be classified into analytical Groups in systematic Group analysis, as in Table 8.2:

Table 8.2. Classification of rare elements into analytical-Groups

Group	Metal precipitated	Precipitated as
Group-I	W	$\text{WO}_3 \cdot x\text{H}_2\text{O}$
Group-II	Mo, V	Sulfides
Group-III	Be, Ti, Zr, Ce, Th, U	Hydroxides

it is, however, more convenient to detect these elements by their characteristic individual tests.

8.2. Reactions of Beryllium (Be^{II})

Beryllium compounds are highly **POISONOUS**. Be^{2+} ion shows certain similarity with Mg^{2+} and Al^{3+} ions (*diagonal relationship*). BeO is an insoluble material. Chloride, sulfate and nitrate salts of Be^{2+} exist as hydrated salts or oxo acids, eg, $[\text{Be}(\text{H}_2\text{O})_4]\text{X}_2$, where, $\text{X} = \text{Cl}^-$, NO_3^- , $\frac{1}{2}\text{SO}_4^{2-}$. Due to very high ionic potential of Be^{2+} ion, $\text{Be}(\text{aq})^{2+}$ ion, i.e, $\text{Be}(\text{H}_2\text{O})_4^{2+}$ ion is moderately acidic ($pK_{\text{Be}}^{\text{H}} \sim 6.52$ at 25°C).

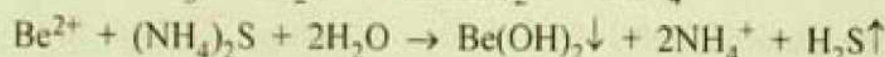
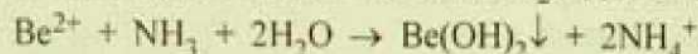
Indication

There is no characteristic indicative test for Be on solid sample.

Reactions of Be^{2+} ion in solution

(1) Aqueous ammonia or ammonium sulfide solution

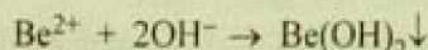
White precipitate of beryllium hydroxide $\text{Be}(\text{OH})_2$ appears (similarity to Al^{3+}).



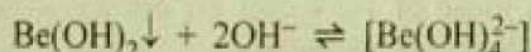
The precipitate is insoluble in excess of the reagent, but it readily dissolves in dil.HCl, tartaric acid and oxalic acid.

(2) Sodium hydroxide solution

White gelatinous precipitate of beryllium hydroxide appears at first.



The precipitate dissolves in excess of NaOH solution, due to the formation of tetrahydroxy beryllate complex, $[\text{Be}(\text{OH})_4]^{2-}$, ion (similarity to Al^{3+}).



Precipitate of $\text{Be}(\text{OH})_2$ is soluble in 10% sodium bicarbonate solution (distinction from Al^{3+}), but insoluble in 1M solution of ethyl amine in which $\text{Al}(\text{OH})_3$ is moderately soluble. Precipitation of $\text{Be}(\text{OH})_2$ does not take place in presence of citrate and tartarate due to complex formation of these ligand anions with Be^{2+} ion.

(3) Ammonium carbonate solution

White precipitate of basic beryllium carbonate appears at first, and the precipitate dissolves in excess of the reagent (distinction from Al^{3+}), but reappears on boiling.

(4) Oxalic acid (or, Ammonium oxalate) solution

No precipitation (distinction from Zr, Ce, Th salts).

(5) Sodium thiosulfate solution

No precipitation (distinction from Al^{3+}).

Confirmation

(1) Basic beryllium acetate-chloroform test

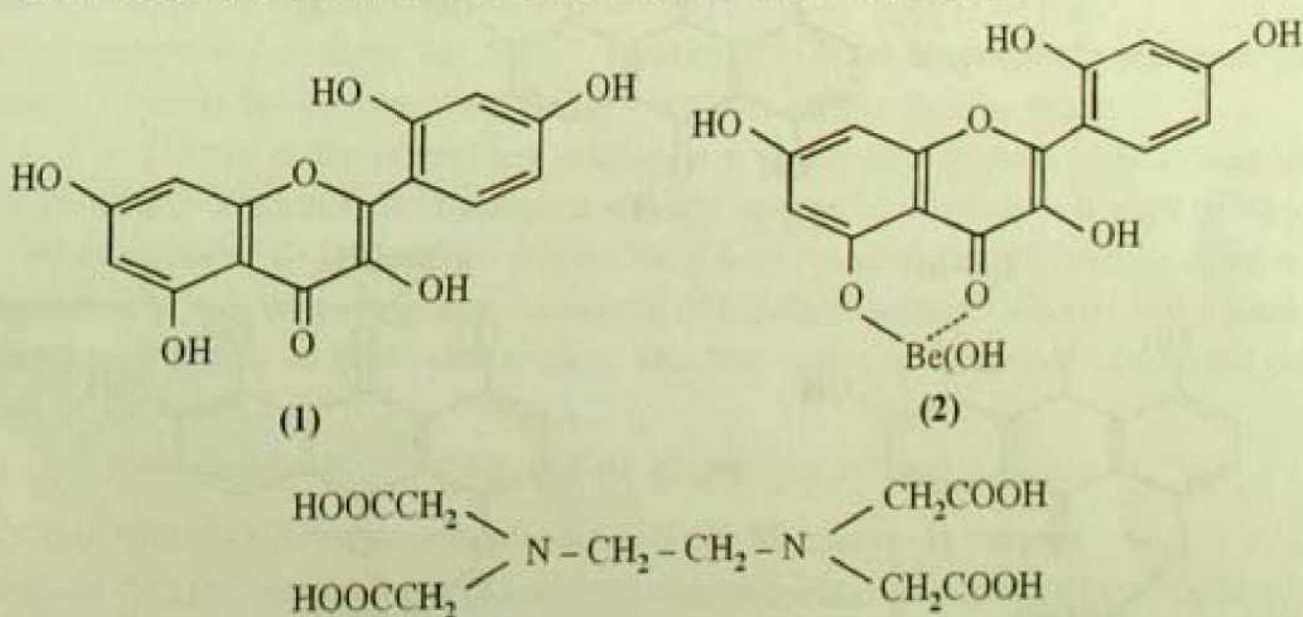
Take 1-2 drops of the test solution in a semi-micro test tube, add drops of (1:1) aq-NH_3 to precipitate $\text{Be}(\text{OH})_2$ completely, centrifuge and discard the centrifugate. Dissolve the precipitate in minimum volume of glacial acetic acid and evaporate the solution to dryness (inside a *FUME CUPBOARD*). The residue is basic beryllium acetate, $\text{BeO} \cdot 3\text{Be}(\text{CH}_3\text{COO})_2$. Cool the residue to room temperature, add a few drops of chloroform and shake. The precipitate dissolves in chloroform (distinction from Al^{3+}). This offers a means of separating Be^{2+} from Al^{3+} .

(2) Reaction of $\text{Be}(\text{OH})_2$ with morin reagent

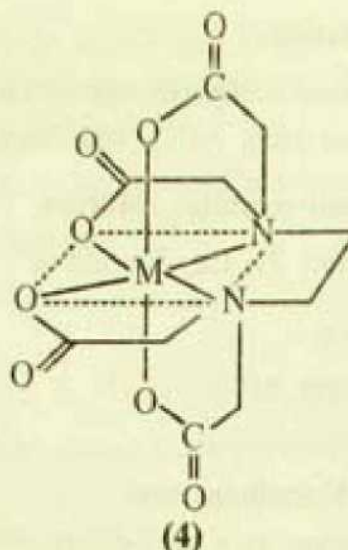
Reagents: (i) 0.02% solution of morin in acetone.

(ii) Cold saturated solution of $\text{Na}_2\text{EDTA} \cdot 2\text{H}_2\text{O}$ in (1:10) aq-NH_3 solution.

Alkaline solution of beryllate reacts with morin reagent (1) to produce a water soluble compound of unknown composition [probably an adsorption compound, (2), similar to that formed with Al^{3+}] is formed, which gives a yellow green fluorescence under $u-v$ light. Sparingly soluble hydroxides of other metals interfere, but may be masked by complex formation with EDTA (3). In presence of EDTA, only $\text{Be}(\text{OH})_2$ is precipitated by aq-NH_3 solution, whereas, the other metal ions remain in solution as their EDTA complexes (4).



(3)



Place 1 drop of the neutral or weakly acidic test solution on a spot plate, add 3 drops of EDTA reagent, one drop of 0.02% acetone solutions of morin reagent and finally one drop of conc. NH_3 solution. Filter the precipitate through a piece of drop-reaction paper and wash the paper consecutively with EDTA solution, water, then with a little acetone. Examine the filter paper under *uv* light. A greenish yellow fluorescing zone is visible.

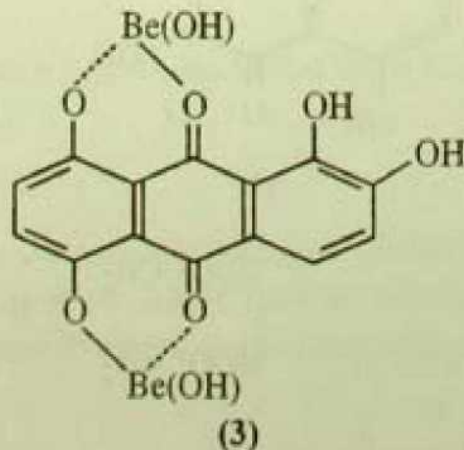
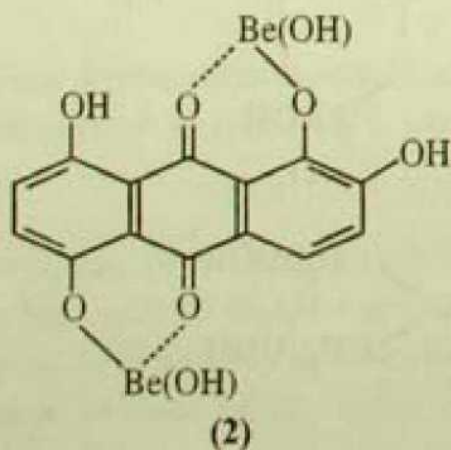
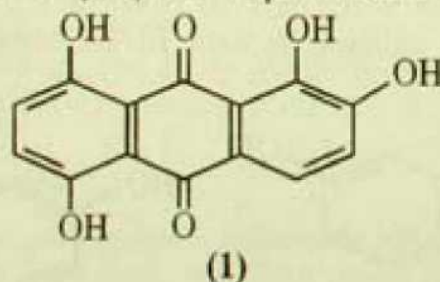
Limit of identification: 0.07% of Be

Limit of dilution: $1:7.1 \times 10^5$

(3) Test with quinalizarin

Reagent: Saturated ethanolic solution, or, freshly prepared 0.05% solution of quinalizarin in 0.1 N NaOH solution.

In ammoniacal or caustic alkaline medium, Be^{2+} salts react with rose violet solution of quinalizarin (1, 2, 5, 8-tetrahydroxy anthraquinone) (1) to produce a blue-violet precipitate or coloration due the formation of (2:1) Be^{2+} : quinalizarin complexes. (2, 3).



Due to the presence of phenolic-OH groups, the complexes (2, 3) dissolve in caustic alkali. The Be^{2+} quinalizarin complex is so stable that it is even formed when alkali beryllium fluoride (fluoraberyllate), $[\text{BeF}_4^{2-}]$ ion reacts with the reagent. Although the ammoniacal solution of the free dye stuff is decolourised by oxidizing agent like Br_2 -water, its $\text{Be}(\text{II})$ complex is resistant to oxidation and decolourization.

Aluminium, zirconium, cerium, thorium interfere by forming adsorption compounds with the dye stuff, and should be removed. But small amounts, of aluminium, lead, zinc and antimony however, do not interfere. Copper, nickel, cobalt and metals forming sparingly soluble hydroxides should be removed. $\text{Fe}(\text{III})$ may be masked with tartarate. Mg^{2+} also gives a blue compound with quinalizarin, but unlike the $\text{Be}(\text{II})$ – quinalizarin complex, $\text{Mg}(\text{II})$ – quinalizarin complex is unstable in ammoniacal medium towards oxidizing agent, such as Br_2 – water.

Mix one drop of the test solution with a drop of freshly prepared solution of quinalizarin in 0.1N NaOH solution on a spot plate. Depending upon the amount of Be^{2+} present a blue colour or, a blue precipitate is produced. Compare with a blank.

Note: For very small amount of beryllium, use an alcoholic solution of the reagent and add a drop of ammonia or NaOH.

Limit of identification: 0.14γ of Be.

Limit of dilution: 1: 3.5×10^5

Detection of Be^{2+} in presence of Mg^{2+}

Reagent: 0.05% quinalizarin in 2 M ammonia solution.

Both Be^{2+} and Mg^{2+} produce blue precipitate, or, colouration with quinalizarin reagent in alkaline solution, but stabilities of the resulting complexes towards oxidizing agents are different.

(i) *In NaOH medium:* Br_2 -water destroys the blue coloured $\text{Be}(\text{II})$ - quinalizarin complex, but the corresponding $\text{Mg}(\text{II})$ complex persists longer.

(ii) *In ammoniacal medium:* The $\text{Mg}(\text{II})$ quinalizarin complex is completely destroyed by Br_2 -water, whereas, the corresponding $\text{Be}(\text{II})$ - complex retains its blue colour.

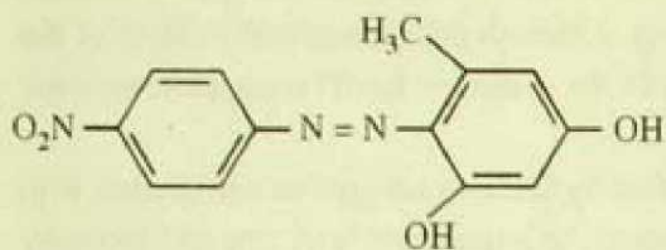
Take 1 to 2 drops of the neutral test solution in a semi-micro test tube, add 2 drops of 0.05% quinalizarin reagent in 2 M ammonia solution. A deep blue colouration appears. Now add 1 ml of saturated Br_2 -water. The original deep blue colour fades, but remains more or less permanently blue, depending upon the amount of beryllium present. Compare with a blank containing only a drop of Mg^{2+} salt solution. The blue colour is completely discharged on addition of Br_2 -water.

Limit of identification: 10 γ of Be in presence of 1000 γ of Mg.

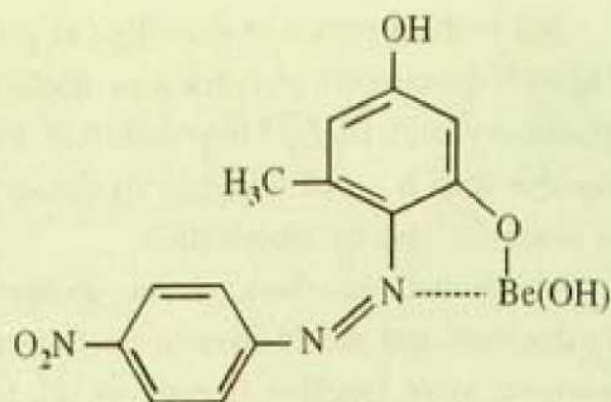
(4) Test with 4-(4-Nitrophenylazo)resorcinol (or Magneson-I) reagent

Reagent: 0.025% solution of 4 (4-nitrophenylazo)resorcinol in 1M NaOH.

The yellow alkaline solution of 4-(4-nitrophenylazo) resorcinol (or Magneson-I) reagent (1) reacts with $\text{Be}(\text{OH})_2$ to form a redish-brown lake (2).



(1)



(2)

The reagent (1) reacts with Mg(II) salts to produce a brownish yellow precipitate, but it is without action on the salts and hydroxides of lanthanide elements. Aluminium and other alkaline earth metal ions do not interfere in the test of beryllium. Zn(II), Co(II), Ni(II), Cd(II), Ag(I) are precipitated as hydroxides under the condition of the experiment, but they may be kept in solution as their cyano complexes by adding a few drops of KCN solution (**CAUTION POISON**) if they are present.

Place a drop of the alkaline reagent solution on a drop reaction paper and add using a capillary tube, a small drop of the test solution at the middle of reagent spot in such a manner that the liquid runs slowly into the paper. Add a further drop of the reagent. In presence of beryllium, an orange or redish-brown fleck is formed at the centre of the spot.

Limit of identification : 0.2γ of Be

Limit of dilution: 1 : 2×10⁵.

8.3 Reactions of Titanium (Ti^{IV})

Most stable and common oxidation state of Ti is Ti(IV) and its compounds are white coloured. TiO₂ occur naturally along with Al₂O₃, Fe₂O₃ and SiO₂ in *bauxite* ore. Ti⁴⁺ (d⁰) ion is colourless in aqueous solution. Ti³⁺ (d¹) maybe produced by reduction of Ti⁴⁺ by strong reducing agents like Zn-amalgam, but Ti³⁺ is readily oxidized to Ti⁴⁺ by air. Ti⁴⁺ ion may exist only in strogly acidic solution. Ti⁴⁺(aq) ion readily hydrolyzes to form titanyl (TiO²⁺) ion on lowering the acidity of the solution, finally hydrated titanium oxide, TiO₂.xH₂O (amorphous) is precipitated around pH = 0~1.

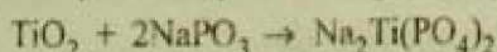
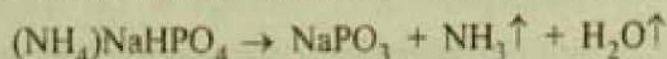


Commonly available titanium compounds include: TiO₂, FeTiO₃, CaTiO₃, Mg₂TiO₄, etc.

Indication

(1) Microcosmic salt bead test

Form a transparent bead of microcosmic salt (NH₄)NaHPO₄ on a platinum wire loop by heating the wire to dull redness and then by adhering some powdered microcosmic salt with it and then heating again. A colour less transparent bead of sodium metaphosphate (NaPO₃) thus formed, dissolves in molten condition, even insoluble TiO₂.



Adhere a minute quantity of the powdered solid sample with the red hot bead and then heat the same first in the oxidizing flame and then in the reducing flame. Observe the colour of the bead when it is hot and then when it is cold. In presence of titanium salt, the following colours of the bead will be observed:

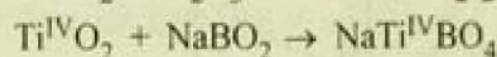
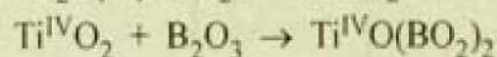
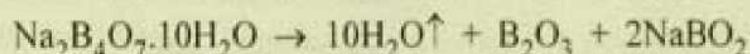
- (i) *Oxidizing flame*: Colourless when hot and cold,
- (ii) *Reducing flame*: Yellow when hot and violet when cold.
- (iii) Heat the bead in the reducing flame with a minute amount of stannous chloride. The bead readily turns violet as Sn(II) reduces Ti(IV) to Ti(III) pyrophosphate,



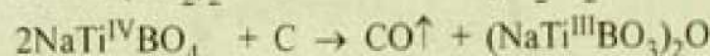
(2) Borax bead test

Titanium salts respond to borax bead test. Following colouration of the borax bead is observed if titanium is present:

- (i) *Oxidizing flame*: Yellow when hot, colourless when cold.



- (ii) *Reducing flame*: Grey when hot, pale violet when cold.

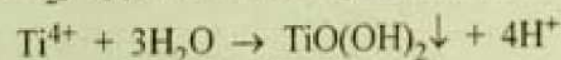


Note: Borax bead test on the reducing flame may also be performed by mixing small amount of (i) SnCl_2 and (ii) FeSO_4 , or, Mohr's salt as in the microcosmic salt bead test.

Reactions of Ti(IV) or Titanyl (TiO^{2+}) ion in solution

(1) Water

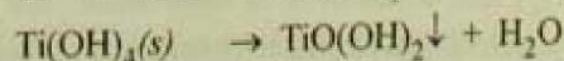
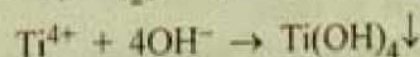
When an aqueous solution of Ti(IV) salt is boiled, white precipitate of metatitanic acid, H_2TiO_3 [$\equiv \text{TiO}(\text{OH})_2$] appears and the supernatant solution becomes strongly acidic.



The precipitate of $\text{TiO}(\text{OH})_2$ is sparingly soluble in dilute mineral acids. The precipitation is inhibited in presence of tartarate, citrate, EDTA and NH_4HF_2 etc. due to complexation (masking) of Ti(IV) with these reagents.

(2) Basic reagents : NaOH , NH_3 , $(\text{NH}_4)_2\text{S}$ solutions

White gelatinous precipitate of orthotitanic acid, H_4TiO_4 [or, titanium hydroxide, $\text{Ti}(\text{OH})_4$] appears when a Ti(IV) salt solution is treated with any of these reagents in the cold. Metatitanic acid, H_2TiO_3 [$\equiv \text{TiO}(\text{OH})_2$] is precipitated from the hot solution:



(3) Disodium hydrogenphosphate solution

White precipitate of titanium monohydrogen phosphate, $\text{Ti}(\text{HPO}_4)_2$, appears even in dilute acidic (HCl , HNO_3 , H_2SO_4) solution:

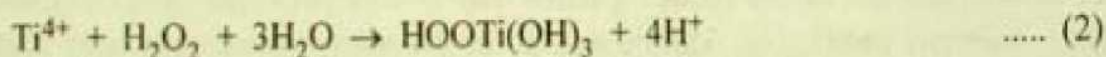
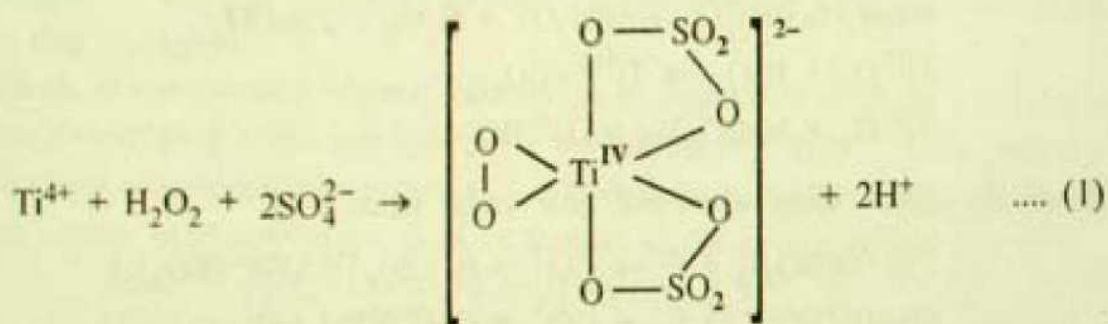


Note: $\text{Ti}(\text{HPO}_4)_2$ is sparingly soluble in water. It is precipitated even in acidic solution (distinction from most metals, whose phosphates are soluble in acidic medium but precipitates in ammoniacal medium, and similarity to zirconium).

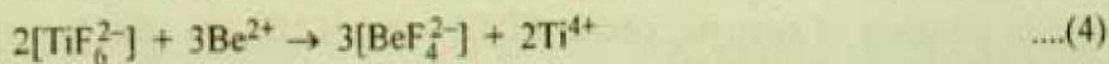
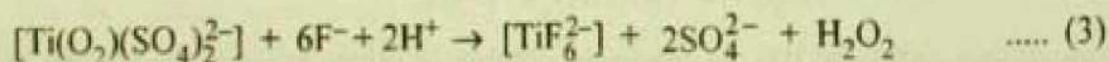
Confirmation

(1) Hydrogen peroxide

In dilute acidic (H_2SO_4) solution, $\text{Ti}(\text{IV})$ salts react with H_2O_2 giving yellow colouration due to the formation of peroxodisulfatotitanic acid, $(\text{H}^+)_2[\text{Ti}(\text{O}_2)(\text{SO}_4)_2]^{2-}$, (1), or, peroxotitanic acid, $\text{HOO-Ti}(\text{OH})_3$ (2).



The yellow colour is discharged by addition of soluble fluoride salts (NH_4HF_2 , NH_4F , NaF , etc) due to the formation of hexafluorotitanate (IV) ion, $[\text{TiF}_6]^{2-}$ (3). But the yellow colour reappears on addition of a soluble beryllium salt (4) and also on digesting with boric acid (5). [distinction from vanadium, which gives wine-red colouration with H_2O_2 under the same condition]



Higher stability of $[\text{BeF}_4]^{2-}$ and BF_3 over $[\text{TiF}_6]^{2-}$ complex due to higher covalency of Be-F and B-F bonds arising from very strong polarizing effect of very small Be^{2+} and $\text{B}(3+)$ ions as compared to Ti^{4+} ion for reactions (4) and (5) and in addition, volatility of molecular BF_3 in reaction (5) drive these reactions from left to right.

Place 1 ml of slightly acidic (H_2SO_4) test solution in a semi-micro test tube and add a few drops of 3% H_2O_2 solution. A yellow colour develops if titanium is present. Add a crystal of NH_4HF_2 , or NH_4F or NaF and shake. The yellow colour is discharged.

Now divide this colourless solution into two parts and perform the following tests:

(i) Add a few drops of beryllium chloride (or sulfate) solution to one part of the colourless solution. The yellow colour reappears.

(ii) To another part of the colourless solution add a small amount of boric acid and slightly warm the mixture on a hot water bath (Fig. 3.15). The yellow colour reappears.

Chromate (itself is yellow), vanadate, molybdate, cerium give coloured reactions with H_2O_2 and should be absent. With iron salts, H_2O_2 gives a violet colouration, which may be discharged by adding syrupy phosphoric acid. Large amount of nitrate, chloride, bromide, coloured ions reduce the sensitivity of the test. Iodide should be removed before applying this test, since, iodide is oxidized to liberate iodine (or I_3^-) which imparts brown colouration to the solution.

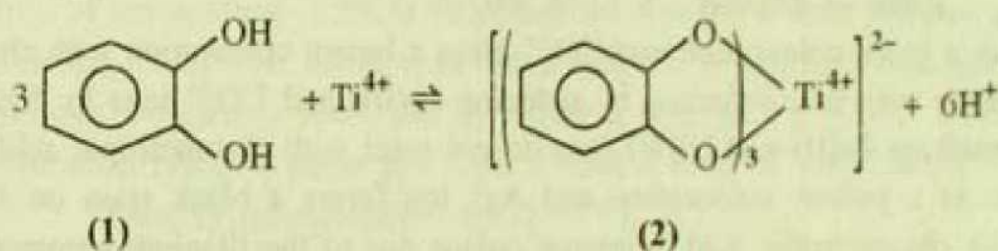
Limit of identification : 2γ of Ti.

Limit of dilution : 1 : 2.5×10^4 .

(2) Test with Pyrocatechol (or, Catechol)

Reagent: Freshly prepared 10% aqueous solution of pyrocatechol.

Ti(IV) salts react with pyrocatechol (1, 2-dihydroxybenzene) (1) in weakly acidic medium to produce a yellowish red colouration due to the formation of Ti(IV)-pyrocatechol chelate complex anion (2).



The colour is not formed if large amount of mineral acid is present. Fe(III) should be absent since it also gives coloured reaction with the reagent. Number of other elements interfere with this reaction. Therefore, this test may be applied after separation of titanium from other metals.

Place a drop of the dilute acidic (H_2SO_4) test solution on a drop reaction paper impregnated with the pyrocatechol reagent. A more or less intense yellow-red fleck appears depending upon the quantity of titanium present.

Limit of identification: 2.7γ of Ti.

Limit of dilution : 1: 1.9×10^4

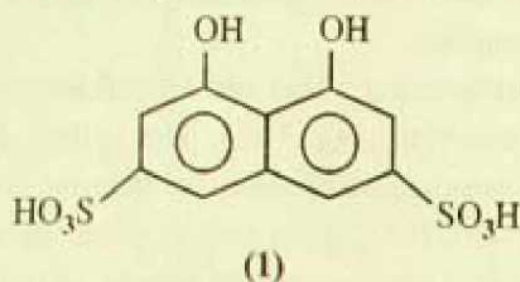
(3) Test with Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid) reagent

Reagent :

(i) Dissolve 0.02g of chromotropic acid in 20 ml of conc. H_2SO_4 by warming. Use freshly prepared solution, since the reagent does not keep well in solution. Or,

(ii) Mix thoroughly 0.1g of disodium salt of chromotropic acid with 5 ml of water and use the clear supernatant solution. The reagent does not keep in solution. Freshly prepared solution should be used.

Chromotropic acid (1,8-dihydroxynaphthalene-3,6-disulfonic acid (**1**)) reacts with titanium (IV) salts in dilute acidic solution to produce a wine-red coloured solution.



In weakly acidic solution ($pH = 2.5 - 5$), a Ti(IV) complex, involving chelation by the phenolic OH groups of the ligand is possibly formed. The intense wine-red colouration probably arise from charge transfer transition of LMCT type. It has also been suggested that in strong H_2SO_4 medium, the reagent (**1**) is oxidized by Ti(IV) to a quinoidal form, which together with the unchanged reagent, coordinate the resulting Ti(III) to produce the wine-red colour.

Place a drop of the test solution in a spot plate or on a drop-reaction paper, and add 1 drop of 5% aqueous solution of disodium salt of the reagent. A red-brown colouration of the solution or a red-brown fleck on the paper appears if titanium is present.

Limit of identification : 3γ of Ti.

Limit of dilution : 1 : 16,700.

Fe (III) gives a green colouration and UO_2^{2+} gives a brown colouration with chromotropic acid. These colours may be discharged by reducing Fe(III) and UO_2^{2+} ions by $SnCl_2$ in HCl medium. The resulting Fe(II) and U(IV) ions do not react with chromotropic acid. Although Hg^{2+} ion produces a yellow colouration and Ag^+ ion forms a black stain on filter paper impregnated with chromotropic acid, wine-red colour due to the titanium chromotropic acid complex is still identifiable. In presence of Fe(III), the brown-red fleck due to the titanium complex appears at the centre of the green stain due to iron.

Detection of titanium in presence of other elements

(i) Place 2-3 drops of the test solution on a watch glass, add 1 drop of $SnCl_2$ solution in HCl (avoiding large excess) and place the watch glass with its contents on a hot water bath, when the precipitate balls together. Impregnate a filter paper strip with chromotropic acid reagent and add a drop of the supernatant liquid from the watch glass with the help of a capillary tube. A wine-red fleck appears if titanium is present.

Alternatively, place the precipitate along with the supernatant liquid on a filter paper. The precipitate remains fixed, whereas, the solution diffuses away. Add a drop of chromotropic acid reagent, a red-brown circle is formed if titanium is present.

(ii) Place 1 drop of the test solution in a micro crucible, add 1 drop of conc. H_2SO_4 , and 5 drops of chromotropic acid reagent. A violet colouration is produced if titanium is present. Compare with a blank.

Large amounts of coloured metallic salts, nitrate and oxidizing agents interfere.

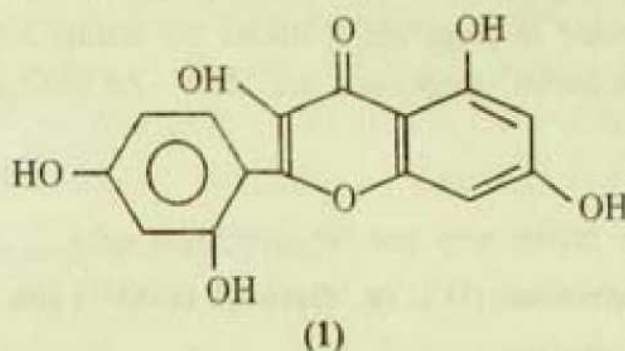
Limit of identification : 0.1γ of Ti.

Limit of dilution : 1 : 5×10^5 .

(4) Test with morin reagent

Reagent. Saturated solution of morin in methanol.

In dilute acidic (H_2SO_4 , HCl , HNO_3) solution, Ti (IV) salts, react with light yellow alcoholic solution of morin (1) to produce an intense brown colouration, probably due to the formation of an anionic chelate complex of Ti(IV) with the reagent. The actual composition of the anionic complex is not known.



Zr(IV) and Th (IV) salts react in similar manner, however, these metal ions may be removed by precipitation with H_3PO_4 . Fe^{III} may be rendered harmless by reducing it to Fe^{II} by thioglycolic acid or Zn/HCl .

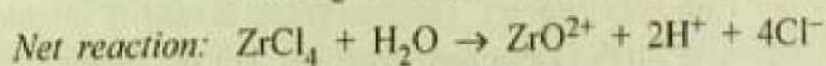
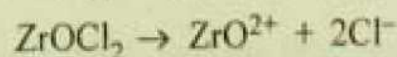
Place a drop of the acidic ($\sim 0.5N$ in HCl) test solution on a drop reaction paper and add 1 drop of saturated methanolic solution of morin reagent. A yellow-brown stain is formed if titanium is present. Perform a blank test by taking a drop of $0.5 N$ HCl instead of the test solution on the drop reaction paper and then adding a drop of the reagent solution.

Limit of identification: 0.01γ of Ti.

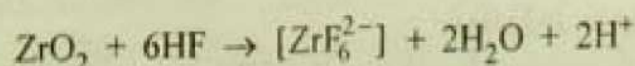
Limit of dilution: $1 : 5 \times 10^6$

8.4 Reactions of Zirconium (Zr^{IV} , ZrO^{2+})

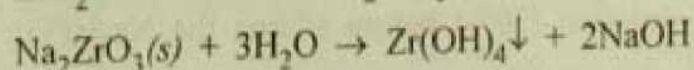
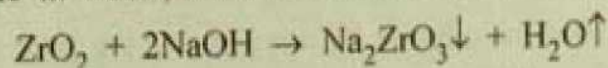
Zr^{IV} is extensively hydrolyzed in aqueous solution giving mainly zirconyl salts containing ZrO^{2+} radical, and rendering the aqueous solution acidic,



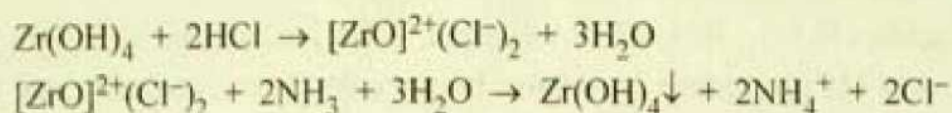
Zr^{IV} readily forms complex with fluoride ion. Insoluble zirconia, ZrO_2 , dissolves in hot hydrofluoric acid, forming $[\text{ZrF}_6]^{2-}$ complex ion,



ZrO_2 dissolves in molten caustic alkali or molten sodium carbonate. The resulting zirconate is almost insoluble in water, as it is transformed into zirconium hydroxide precipitate.



Precipitated zirconium hydroxide dissolves in HCl, but it is again precipitated by *aq*-NH₃ solution,



In presence of large excess of sulfate ion or sulfuric acid, zirconium exists as the anionic complex, $[\text{ZrO}(\text{SO}_4)_2]^{2-}$ ion, as a result, it does not responds to its usual tests. That is why, sulfuric acid should be avoided in preparing solutions for testing zirconium.

Commonly available zirconium compounds are: ZrO_2 , $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, $\text{K}_2[\text{ZrF}_6]$.

Indication

There is no characteristic preliminary test for zirconium salts.

Reactions of Zirconium (IV), or, Zirconyl (ZrO^{2+}) ion in solution

(1) Sodium hydroxide solution

(i) NaOH solution in cold

Gelatinous white precipitate zirconium hydroxide Zr(OH)_4 , or, hydrated zirconium oxide, $(\text{ZrO}_2 \cdot x\text{H}_2\text{O})$ appears in the cold. The precipitate is insoluble in excess of NaOH solution (distinction from beryllium and aluminium), but it is soluble in dilute mineral acids (HCl, HNO_3 , avoid H_2SO_4).

(ii) Hot NaOH solution

White precipitate of $\text{ZrO}(\text{OH})_2$ appears, the precipitate is sparingly soluble in dilute mineral acids but soluble in concentrated mineral acids.

Fluoride, citrate and tartarate inhibit precipitation of zirconium (IV) hydroxide by forming complexes with the metal ion.

(2) Aqueous ammonia or ammonium sulfide solution

White gelatinous precipitate of zirconium hydroxide Zr(OH)_4 (or, $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$) appears. The precipitate is insoluble in excess of the reagents, but soluble in dilute mineral acids (HCl, HNO_3 , avoid H_2SO_4).

(3) Ammonium carbonate solution

White precipitate due to basic zirconium carbonate appears. The precipitate is readily soluble in excess of the reagent due to the formation of Zr(IV) carbonato complex, but the precipitate reappears on boiling the solution.



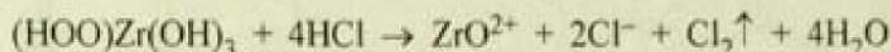
(4) Disodium hydrogenphosphate solution

White precipitate of zirconium hydrogenphosphate, $\text{Zr(HPO}_4)_2$, or, $\text{ZrO(H}_2\text{PO}_4)_2$ appears even in presence of 10% H_2SO_4 by weight and also in presence of tartarate and citrate. Only titanium and zirconium phosphates are precipitated under these conditions. Zirconium phosphate alone may be precipitated keeping titanium in solution by complexing the later as peroxotitanic acid by adding sufficient H_2O_2 solution (30%) before adding the Na_2HPO_4 solution.

(5) Hydrogen peroxide (H_2O_2)

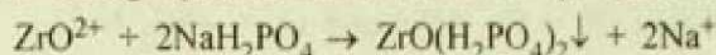
(i) H_2O_2 alone

White precipitate of peroxozirconic acid, $(\text{HOO})\text{Zr}(\text{OH})_3$, appears from slightly acidic solutions. If the precipitate is warmed with conc. HCl , chlorine is liberated.



(ii) H_2O_2 and Na_2HPO_4 mixture

Precipitate of zirconium hydrogenorthophosphate, $\text{Zr}(\text{HPO}_4)_2$, or, $\text{ZrO}(\text{H}_2\text{PO}_4)_2$ is formed even if the solution is slightly acidic and also in the presence of citrate and tartarate.



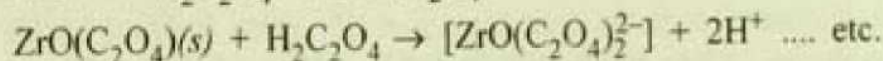
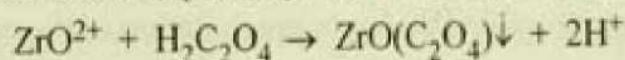
(6) Saturated potassium sulfate solution

White precipitate of potassium zirconyl sulfate $\text{K}_2[\text{ZrO}(\text{SO}_4)_2]$ appears. The precipitate does not dissolve in excess of the reagent. If the reaction is carried out under boiling condition, white precipitate of basic zirconium sulfate (ZrOSO_4 or $\text{Zr}(\text{OH})_2\text{SO}_4$) appears, which is insoluble in dil. HCl (distinction from Ce and Th).

Note: No precipitate is formed if sodium sulfate is used instead of potassium sulfate.

(7) Oxalic acid solution

White precipitate of zirconyl oxalate appears. The precipitate is soluble in excess of oxalic acid, or, ammonium oxalate, possibly due to complex formation (distinction from Th).



(8) Ammonium oxalate solution

White precipitate of zirconyl oxalate, $\text{ZrO}(\text{C}_2\text{O}_4)$ appears. The precipitate is soluble in excess of the reagent due to complex formation (distinction from Be and Al).



Note: Neither oxalic acid nor ammonium oxalate can form any precipitate in presence of sulfuric acid or large excess of sulfate ion, as zirconium exists as the anionic complex, $[\text{ZrO}(\text{SO}_4)_2]^{2-}$ ion under these conditions.

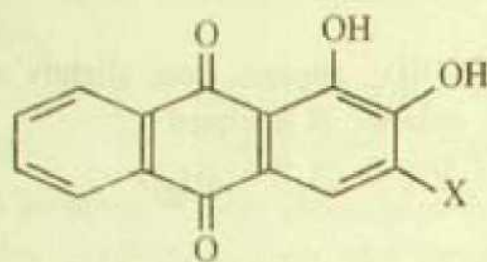
Confirmation

(1) Test with alizarin or alizarin-S

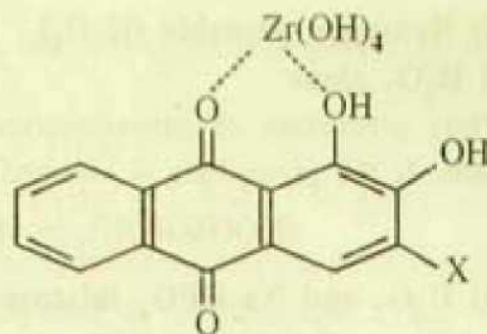
Reagent : (i) *Alizarin*: Saturated solution in 95% ethanol.

(ii) *Alizarin-S*: 2% solution in water.

In weakly acidic (dil. HCl) solution $\text{Zr}(\text{IV})$ salts react with alizarin or alizarin-S (1) to produce red to dark violet precipitate, which is an adsorption compound or lake (2) of the dye stuff with zirconium hydroxide $\text{Zr}(\text{OH})_4$.



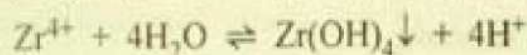
(1)



(2)

Alizarin ($X = H$), Alizarin-S ($X = -SO_3^-Na^+$)

In weakly acidic solution Zr^{4+} is extensively hydrolyzed with precipitation of $Zr(OH)_4$,



The hydrolytic equilibrium remains extensively right shifted due to removal of $Zr(OH)_4$ in the form of the lake (2). The same red-violet lake results on precipitation of $Zr(OH)_4$ by $aq.NH_3$ in presence of the reagent (1). The zirconium-alizarin lake (2) is stable in dil.HCl. In strong HCl medium Zr(IV) forms a fairly stable hydrosol.

Fluoride and sulfate ions form more stable complexes $[ZrF_6]^{2-}$ and $[ZrO(SO_4)_2]^{2-}$ and phosphate form precipitates of $ZrO(H_2PO_4)_2$ or, $Zr(HPO_4)_2$ with Zr(IV). Thus F^- , SO_4^{2-} and PO_4^{3-} ions lower the sensitivity of this test for Zr(IV). Organic hydroxy acids, molybdate, and tungstate ions lower the concentration of Zr(IV) due to precipitation of the corresponding Zr(IV) salts.

Interference due to sulfate maybe eliminated by addition barium chloride, which precipitates sulfate as $BaSO_4$.

Zr(IV) maybe detected in presence of Be(II), Al(III), Ti(IV) and Th(IV) by the following procedure:

Mix a drop of the nearly neutral test solution with a drop of the reagent solution in a micro crucible, or, in a small porcelain basin and heat just to boiling. Red to violet coloured adsorption compound is formed if Zr(IV) and other metals are present. Add a drop of 1N HCl solution. Only the Zr(IV) compound remains unaffected, colour/precipitate due to the other metals disappear in presence of HCl. A deep red, or, violet colour, or, precipitate is formed if zirconium content is high. Only a red fleck appears if zirconium content is low.

Limit of identification: 0.5γ of Zr.

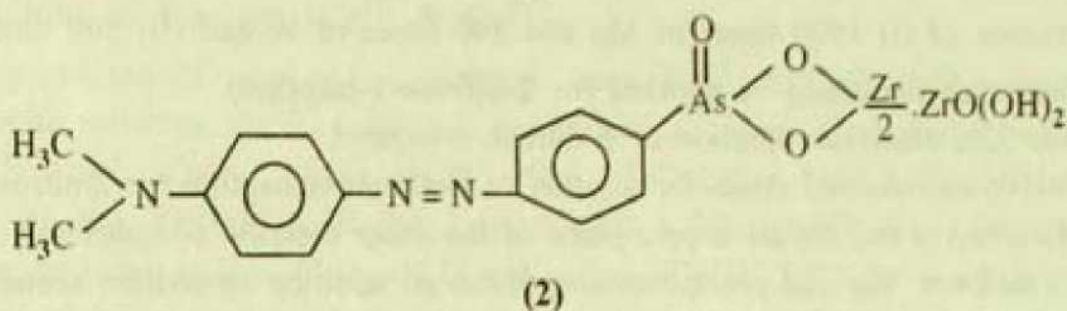
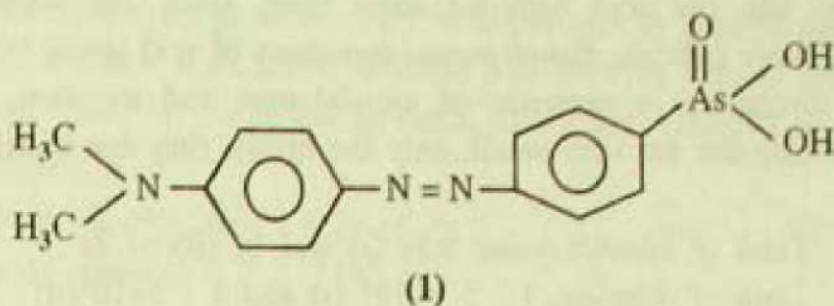
Limit of dilution: 1: 1×10^5

(2) Test with *p*-dimethylaminoazophenylarsonic acid

Reagent: Dissolve 0.1g of *p*-dimethylaminoazophenylarsonic in 100 ml of ethanol containing 5 ml of conc.HCl.

Zr(IV) salts in acidic (HCl, HNO_3 , avoid H_2SO_4) solution react with

p-dimethylaminoazophenyl arsonic acid (1) to give a brown precipitate of Zr(IV) complex (2) of the reagent.



Sensitivity of the test is lowered in the presence of sulfate, fluoride, phosphate ions and organic hydroxy acids, which either precipitate zirconium (IV) or, form soluble complexes with it. Sb(V) interferes by forming a brown colouration like the Zr^{IV} complex, but the colour disappears slowly within 2-3 minutes on treatment with HCl. Sb^{III} gives a slightly coloured fleck, which immediately disappears on bathing the filter paper with dil. H_2SO_4 (or HNO_3). Th(IV) reacts similar to zirconium (IV), but the colour disappears immediately on bathing the filter paper with dilute mineral acids. Stannic acid also gives a brown precipitate with the reagent, but the precipitate is, however, not formed in high concentration of acid and very low concentration of tin (IV).

Impregnate a Whatman No. 41 filter paper strip with the reagent solution and allow to dry. Add a drop of the weakly acidic (HCl, HNO_3 , not H_2SO_4) test solution. A brown stain is produced if zirconium is present. Now bath the filter paper strip in 2N HCl solution at 50-60°C. As the unreacted reagent on the filter paper is washed away by the acid, the brown fleck, or, ring due to the Zr(IV) complex (2) becomes clearly visible.

Limit of identification: 0.1γ of Zr.

Limit of dilution: 1: 5×10^5

Titanium (IV), molybdate and tungstate also give red-brown acid-resistant flecks on filter paper strips impregnated with *p*-dimethylaminoazophenylarsonic acid (1). Interference due to these ions may be eliminated by treating the test solution with H_2O_2 , thereby, transforming these ions into their peroxo compounds, which practically do not react with the reagent.

Mix 2-3 drops of the test solution (which may contains $Zr(IV)$, $Ti(IV)$, MoO_4^{2-} , WO_4^{2-}) with 1 drop of conc. HCl and a drop of 30% H_2O_2 on a spot plate. Place a drop of this mixture on a Whatman No. 1 filter paper strip impregnated with *p*-dimethylaminoazophenylarsonic acid reagent. Now bath the filter paper strip in warm conc. HCl, when a red fleck appears at the

middle of the moist spot and disappears soon after. If zirconium is present, a brown ring appears around the fleck. Stains due to molybdate and tungstate may still remain even after keeping the paper dipped into the acid bath for some time, since zirconium (IV) may induce coprecipitation of these radicals. Simultaneous formation of acid stable brown ring with a red centre indicates zirconium in presence of molybdenum and tungsten. If the amounts of molybdenum and tungsten are very small, only the brown ring due to zirconium complex is visible.

Limit of identification: 0.5γ (i) and 1γ (ii) of Zr

Limit of dilution: 1 : 5×10^4 (i) and 1 : 5×10^4 (ii)

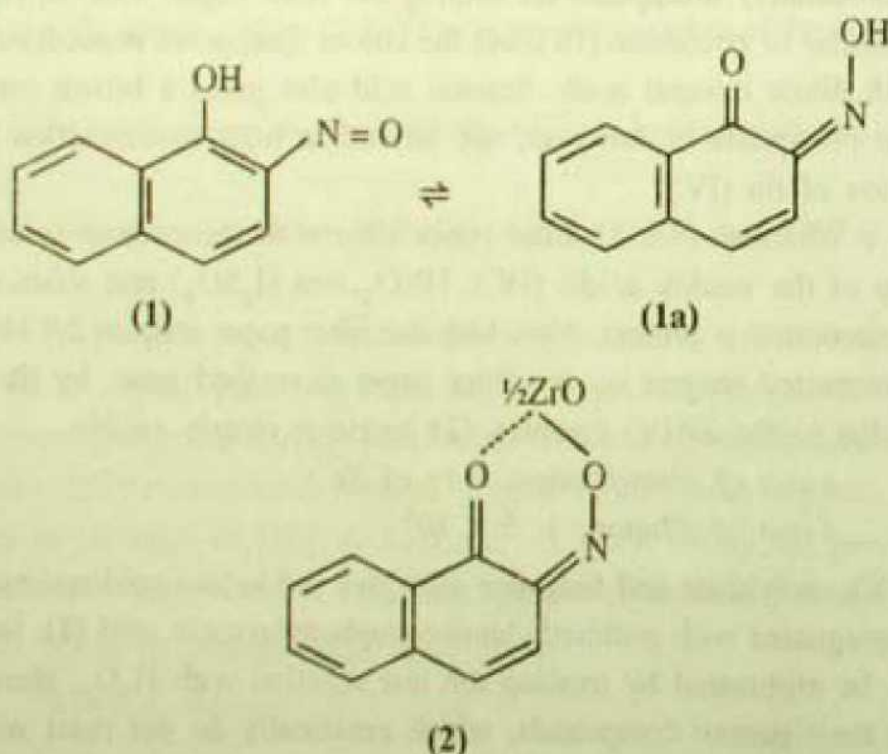
in presence of (i) 1000 times of Mo and 500 times of W and (ii) 500 times of Ti.

(3) Test with β-nitroso- α-naphthol (or 2-nitroso-1-naphthol)

Reagent: 2% alcoholic solution of β-nitroso-α-naphthol.

Yellow-brown coloured ethanolic solution of β-nitroso-α-naphthol (or 2-nitroso-1-naphthol, 2N1N) (1) forms a red coloured precipitate of the inner metallic complex salt with Zr(IV) in dil.HCl medium. The red precipitate coagulates on addition of sodium acetate. α-Nitroso-β-naphthol gives a greenish-yellow compound with Zr(IV).

The complex formation of nitroso naphthols (1) with metal ions probably does not involve deprotonation of the phenolic-OH group, which possibly tautomerises with the nitroso group to transform the ligands into their quinoidal oxime forms (1a). The oxime (=NOH) function deprotonates during complex formation, producing inner metallic complexes (2).



Impregnate a strip of Whatman No. 1 filter paper with the reagent solution and then add 1 drop of the hydrochloric acid test solution. A more or less intense red fleck is formed on the yellow-brown back ground of the reagent paper, depending upon the amount of Zr(IV) present. Add drops of dil.HCl, the spot becomes clearly visible.

Sulfate and fluoride lower the sensitivity of the test by lowering the concentration of zirconium (IV) due to the formation of sulfato- and fluoro-complexes, $[\text{Zr}(\text{SO}_4)_3]^{2-}$ and $[\text{ZrF}_6]^{2-}$ respectively. Interference due to sulfate may be eliminated by precipitating sulfate as BaSO_4 by treating the test solution with BaCl_2 solution and fluoride can be rendered harmless by transforming it into $[\text{BeF}_4]^{2-}$ ion by adding BeCl_2 solution, as $[\text{BeF}_4]^{2-}$ complex is more stable than $[\text{ZrF}_6]^{2-}$ complex.

Limit of identification : 0.2% of Zr.

Limit of dilution: 1 : 2.5×10^5

8.5 Reactions of Cerium (Ce^{III} & Ce^{IV})

Cerium compounds occur in two oxidation states, Ce^{III} and Ce^{IV} . Ce^{III} compounds are in general white, whereas, Ce^{IV} compounds are yellow in colour. Commonly available cerium compounds are: CeO_2 , $\text{CeO}_2 \cdot x\text{H}_2\text{O}$, CeF_4 , $\text{Ce}(\text{NO}_3)_4 \cdot 2\text{NH}_4\text{NO}_3$, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4$, $\text{Ce}_2(\text{SO}_4)_3 \cdot 3\text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ etc. CeO_2 is white when pure, hydrated oxides, $\text{CeO}_2 \cdot x\text{H}_2\text{O}$, are yellow. $[\text{Ce}(\text{H}_2\text{O})_9]^{4+}$ ion is a fairly strong acid and it has a profound tendency to form complexes with anions of the acids in which it exists. As a result of this, the formal potentials of $\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}}$ couple depends upon the nature of the acid medium, as shown below.

Medium:	1M HClO_4	1M HNO_3	1M H_2SO_4	2M HCl
$E^\circ(\text{Ce}^{\text{IV}}/\text{Ce}^{\text{III}})$ Volt:	+1.70	+ 1.61	+ 1.44	+ 1.28

Indication

(1) Borax-bead test

Ce compounds respond to borax bead test.

Oxidizing flame: Dark-brown when hot and light yellow to colourless when cold.

Reducing flame: Colourless when hot and cold.

Reactions of Ce^{III} and Ce^{IV} ions in solution

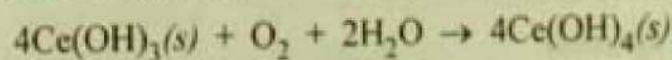
Ce^{IV} may be obtained in solution by oxidation of Ce^{III} by strong oxidants, viz, peroxodisulfate, bismuthate in HNO_3 medium. Ce^{IV} is similar to Ti^{IV} and Zr^{IV} in its reactions. Ce^{IV} - phosphate is insoluble in 4N HNO_3 and iodate is insoluble in 6N HNO_3 .

(1) Ammonia or Sodium hydroxide solution

Ce^{III} : White precipitate of Ce^{III} hydroxide, $[\text{Ce}(\text{OH})_3]$, or $\text{Ce}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ appears. The precipitate is insoluble in excess of the reagents.

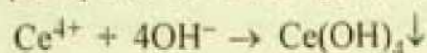


The white precipitate of $\text{Ce}(\text{OH})_3$ is eventually transformed to yellow coloured Ce^{IV} hydroxide due to aerial oxidation.

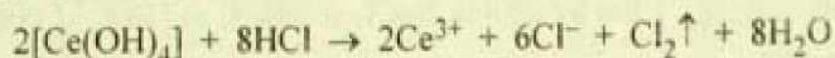


Precipitation is hindered by the presence of complex forming ions, eg. tartarate, citrate etc.

Ce^{IV}: Yellow precipitate of ceric hydroxide, Ce(OH)₄, appears.



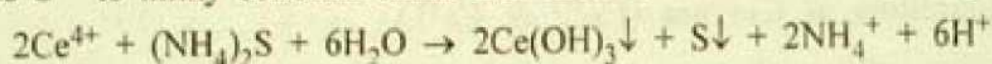
If the precipitate of Ce(OH)₄ is warmed with hydrochloric acid, HCl is oxidized by Ce^{IV} to liberate Cl₂, and Ce^{III} ions are formed.



(2) Ammonium sulfide solution

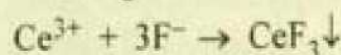
Ce^{III}: Same type of observation as with *aq*-NH₃ and NaOH solutions.

Ce^{IV}: Oxidizes S²⁻ to milky colloidal sulfur and itself is reduced to Ce(III)-hydroxide.

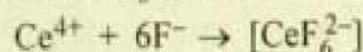


(3) Ammonium fluoride solution

Ce^{III}: White gelatinous precipitate of Ce^{III} fluoride appears, which is transformed to a powdery mass on standing.



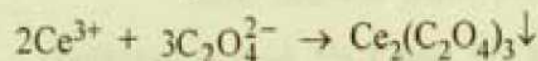
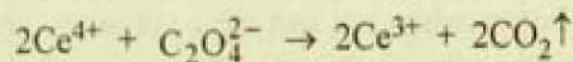
Ce^{IV}: Yellow colour of Ce^{IV} solution disappears due to the formation of soluble complex, hexfluorocerate (IV), [CeF₆²⁻] ion,



(4) Oxalic acid or ammonium oxalate solution

Ce^{III}: White precipitate of Ce^{III} oxalate appears. The precipitate is insoluble in excess of the reagents (distinction from Zr^{IV} and Th^{IV}) and also in very dilute mineral acids.

Ce^{IV}: Yellow colour of Ce^{IV} is discharged as Ce^{IV} is reduced by oxalate ion to Ce^{III} ion, which forms white precipitate of Ce^{III} oxalate,



(5) Potassium iodate (KIO₃) solution

Ce^{III}: In neutral solution Ce^{III} reacts with KIO₃ to produce white precipitate of Ce^{III}-iodate, Ce(IO₃)₃, which is soluble in HNO₃ (distinction from Ce^{IV}).

Ce^{IV}: White precipitate of Ce^{IV} iodate, Ce(IO₃)₄, appears even from conc. HNO₃ test solution (distinction from Ce^{III}). Zr^{IV} and Th^{IV} react similar to Ce^{IV}. Th^{IV} iodate is precipitated even from 50% HNO₃, whereas, Zr^{IV} - iodate dissolves in warm HCl (distinction from Al^{III}).

(6) Saturated potassium sulfate solution

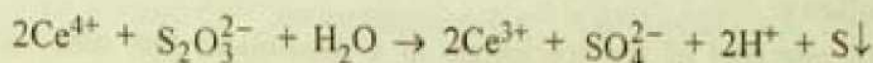
Ce^{III}: White crystalline precipitate of the double salt of composition Ce₂(SO₄)₃·3K₂SO₄ separates in neutral solution. In slightly acidic solution the composition of the precipitate is Ce₂(SO₄)₃·2K₂SO₄·2H₂O (distinction from Al^{III} and Be^{II}).

Ce^{IV}: No precipitation (distinction from Ce^{III})

(7) Sodium thiosulfate solution

Ce^{III}: No reaction (distinction from Th^{IV} and Ce^{IV})

Ce^{IV}: Discharge of yellow colour of Ce⁴⁺ ion with separation of sulfur as Ce^{IV} oxidizes S₂O₃²⁻ ion.



(8) Ammonium carbonate solution

Ce^{III}: White precipitate of Ce^{III} carbonate, Ce₂(CO₃)₃ appears from neutral solution, the precipitate is almost insoluble in excess of the reagent (distinction from Be²⁺, ZrO²⁺ and Th⁴⁺). The precipitate is also insoluble in sodium carbonate solution.

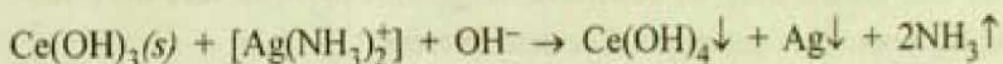
(9) Tests based on oxidation of Ce^{III} to Ce^{IV}

Ce^{III}: Strong oxidants such as sodium bismuthate oxidizes colourless Ce³⁺ ion to yellow Ce⁴⁺ ion in dil. HNO₃ medium in the cold. Potassium or ammonium peroxodisulfate and lead dioxide also oxidize Ce³⁺ to Ce⁴⁺ in 8M HNO₃ under boiling condition.



(10) Ammoniacal silver nitrate solution

Ce^{III}: In neutral solution Ce^{III} salts or hydroxide is oxidized to yellow brown Ce^{IV} hydroxide by ammoniacal silver nitrate solution, which is reduced to finely divided black metallic silver.



Place a drop of the neutral test solution in a small porcelain crucible, add one drop of the reagent and warm the mixture gently on a hot water bath. A black precipitate or a brown colouration appears.

Limit of identification : 1γ of Ce

Limit of dilution : 1 : 5 × 10⁴

Confirmation

Tests based on oxidizing reactions of Ce^{IV}

Yellow colour of Ce⁴⁺ ion is discharged as it is reduced to colourless Ce³⁺ ion by reducing agents, such as H₂S-water, SO₂-water, HI, KI, H₂O₂ and sodium thiosulfate (discussed before).

(1) Anthranilic acid (2-hydroxybenzoic acid) reagent

Ce^{IV} oxidizes anthranilic acid into a brown compound. Ce^{III} does not react with the reagent. Place a drop of the slightly acidic (HNO₃) test solution on a spot plate and add 1 drop of the reagent. A blackish blue precipitate first appears, which readily transforms into a soluble product and the solution turns brown.

Fe (III) inhibits the test, but may be masked with phosphoric acid. Vanadate, chromate also react in the same manner. Reducing agents should be absent.

(2) Separation of Cerium and Thorium

Both the metal ions are precipitated as hydroxide on treatment with a solution of aq-NH₃.

Dissolve the precipitate in 2M HCl and treat the solution with a few crystals of oxalic acid. Both cerium and thorium are precipitated as oxalates. Divide the precipitate into two parts and treat as follows:

Part (i): To one part of the precipitate in a semi-micro test tube, add a buffer solution consisting of ammonium acetate and acetic acid. Thorium oxalate dissolves, but cerium oxalate remains undissolved in the residue.

Part (ii) : To another part of the precipitate add a large excess of ammonium oxalate solution. Thorium oxalate dissolves through formation of soluble oxalato complexes, whereas, cerium oxalate remains undissolved. Centrifuge and treat the centrifugate with HCl. Thorium oxalate is reprecipitated.

(3) Benzidine blue test

Reagent: Dissolve 0.5 g of benzidine or its hydrochloride in 10 ml of acetic acid, then dilute to 100 ml with water.

Like many other oxidizing agents and auto oxidizable substances, Ce^{IV} oxidizes benzidine to benzidine blue (cf. Sect. 4.4). Ce^{III} reacts in the same manner. But the test can not be applied if Mn, Co, Cu, Ag, Tl, Pb and chromate are present, since they also can transform benzidine to benzidine blue. This test for cerium may be applied after separating cerium as cerous fluoride by treating the neutral or slightly acidic test solution with hydrofluoric acid.

Place a drop of the test solution on a drop-reaction paper. Add a drop of dil. NaOH (2M) solution and then a drop of benzidine reagent. A more or less deep blue colouration appears depending upon the quantity of cerium present.

Limit of identification : 0.18% of Ce

Limit of dilution : 1 : 2.75×10^5

(4) Detection of cerium in presence of iron (III)

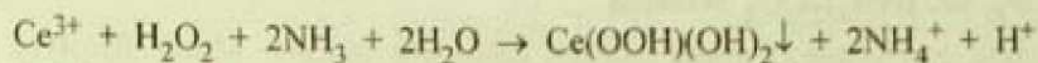
Since benzidine blue test for cerium is conducted in alkaline solution, in which iron (III), if present, is precipitated as brown $\text{Fe}(\text{OH})_3$, it interferes with the detection of cerium. When a mixture of Ce^{III} and Fe^{III} is treated with a soluble fluoride in acidic medium, or, with hydrofluoric acid, Ce^{III} fluoride is precipitated, whereas, Fe^{III} remains in solution as hexafluoroferrate (III) complex, $[\text{FeF}_6]^{3-}$ ion. The precipitated CeF_3 , on treatment with alkali, produces cerous hydroxide, $\text{Ce}(\text{OH})_3$, which is transformed to ceric hydroxide, $\text{Ce}(\text{OH})_4$, by aerial oxidation. $\text{Ce}(\text{OH})_4$ oxidizes benzidine to benzidine blue.

Take 1 ml of the acid (dil. H_2SO_4) test solution (which may contain Ce^{III} and Fe^{III}) in a semi-micro test tube, add a few drops of NaOH solution (2M) until a permanent precipitate is formed. Add a few drops of hydrofluoric acid, boil the mixture for 2-3 minutes and centrifuge. Discard the centrifugate, wash the residue with water by centrifugation. Add 1 drop of NaOH solution (2M) and 1 drop of acetic acid solution of benzidine. A more or less blue colouration appears depending upon the amount of cerium present.

Limit of identification: 70% of Ce in presence of 227 mg of Fe.

(5) Test with $\text{H}_2\text{O}_2\text{-NH}_3$ solution

Ce^{III} and Ce^{IV} react with H_2O_2 in presence of aq-NH_3 solution yielding yellow-brown precipitate consisting of Ce^{III} and Ce^{IV} perhydroxides, $\text{Ce}^{\text{III}}(\text{OOH})(\text{OH})_2$ and $\text{Ce}^{\text{IV}}(\text{OOH})(\text{OH})_3$ respectively:



The test can not be applied in presence of Fe^{III} , as brown precipitate of $\text{Fe}(\text{OH})_3$ obscures the detection of cerium perhydroxides, but it can be applied in presence of other rare earth metal ions. Fe^{III} may be masked by tartarate, citrate etc., but these also lower the sensitivity of cerium detection. Large amounts of coloured ions interfere.

Take 1-2 drops of the test solution in a semi-micro test tube, and 2-3 drops of 3% H_2O_2 and drops of (1:1) aq-NH_3 until alkaline. Warm gently on a hot water bath. A yellow-brown precipitate or colouration appears if cerium is present.

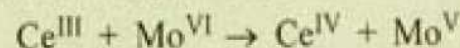
Limit of identification : 0.35γ of Ce

Limit of dilution : 1 : 14.3×10^4

(6) Molybdenum blue test

Reagent: Saturated solution of phosphomolybdic acid in water.

Phosphomolybdic acid, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}] \equiv (\text{H}_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot \text{aq})$ oxidizes Ce^{III} to Ce^{IV} in presence of alkali according to the reaction,



when molybdenum blue results. Zirconium and thorium salts are indifferent toward phosphomolybdic acid. This test may be applied for detection of cerium in presence of other rare earth metals and zirconium and thorium.

Mix 1 drop of the test solution with 1 drop of phosphomolybdic acid solution on a spot plate and add 1 drop of concentrated (~40%) NaOH solution. A more or less blue colouration or a blue precipitate is formed depending upon the cerium content.

Limit of identification : 0.52γ of Ce

Limit of dilution : 1 : 6.1×10^4

8.6 Reactions of Thorium (Th^{IV})

Insoluble thorium oxide or thoria (ThO_2) is the commonly available compound of thorium. Thorium nitrate, $\text{Th}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ is soluble in water. Thorium iodate, $\text{Th}(\text{IO}_3)_4$, is precipitated from 50% HNO_3 and is an insoluble material. Basic chromate, $\text{Th}(\text{OH})_2\text{CrO}_4 \cdot \text{H}_2\text{O}$ and nitrate complexes as, $\text{Mg}[\text{Th}(\text{NO}_3)_6] \cdot 8\text{H}_2\text{O}$ are also known.

Indication

There is no preliminary test which can be applied directly on solid thorium compounds.

Reactions of Thorium (Th^{IV}) ion in solution

(1) Aq-NH_3 , $(\text{NH}_4)_2\text{S}$ or NaOH solution

White precipitate of thorium hydroxide, $\text{Th}(\text{OH})_4$, or, $\text{ThO}_2 \cdot x\text{H}_2\text{O}$ appears. The precipitate

is insoluble in excess of the reagents, but dissolves in dilute mineral acids when freshly precipitated. Precipitation is inhibited in presence of citrate and tartarate due to complex formation.

(2) Na_2CO_3 , or, $(\text{NH}_4)_2\text{CO}_3$ solution

Initially white precipitate of basic thorium carbonate appears, which dissolves in excess of the reagents due to the formation of pentacarbonatothorate (IV) complex, $[\text{Th}(\text{CO}_3)_5]^{6-}$ ion.

(3) Saturated potassium sulfate solution

White precipitate of the complex salt, potassium tetrasulfatothorate (IV), $\text{K}_4[\text{Th}(\text{SO}_4)_4]$ separates out. The precipitate is insoluble in excess of the reagent, but soluble in dil. HCl and HNO_3 .

(4) Hydrogen peroxide

White precipitate of an association compound of thorium dioxide and hydrogen peroxide, $\text{ThO}_2 \cdot 3\text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$, appears in neutral or, slightly acidic solution.

(5) Potassium ferrocyanide solution

In neutral, or, faintly acidic solution, white precipitate of thorium ferrocyanide, $\text{Th}[\text{Fe}(\text{CN})_6]$, separates out.

(6) Potassium fluoride solution

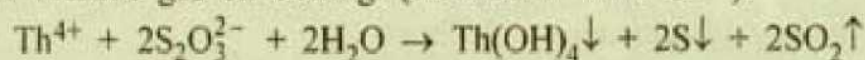
Heavy white precipitate of thorium fluoride, ThF_4 , appears. The precipitate is insoluble in excess of the reagent (distinction from Ti^{IV} , Zr^{IV} , Al^{III} and Be^{II} , offering a method of separation).

(7) Potassium iodate solution

Heavy white precipitate of thorium iodate, $\text{Th}(\text{IO}_3)_4$ is formed even in 50% nitric acid solution (distinction from Ce^{III}).

(8) Sodium thiosulfate solution

White precipitate of thorium hydroxide and colloidal milky elemental sulfur appears with evolution of sulfur dioxide gas on boiling. (distinction from Ce^{IV}).

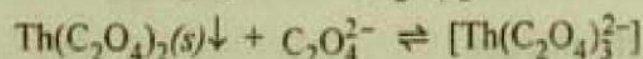


(9) Oxalic acid solution

White precipitate of thorium oxalate, $\text{Th}(\text{C}_2\text{O}_4)_2$, crystallizes out (distinction from Be^{II} and Al^{III}). The precipitate is insoluble in excess of the reagent and also in dilute HCl (~ 0.5M).

(10) Ammonium oxalate

Initially, white precipitate of thorium oxalate, $\text{Th}(\text{C}_2\text{O}_4)_2$, crystallizes out, but on boiling with a large excess of the reagent, the precipitate passes into solution, due to the formation of trioxalato thorate (IV) complex, $[\text{Th}(\text{C}_2\text{O}_4)_3]^{2-}$ ion. White precipitate of thorium oxalate reappears on addition of hydrochloric acid (distinction from Zr^{IV}).

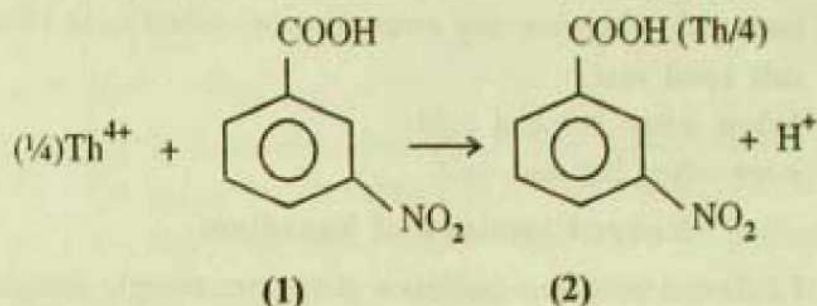


Confirmation

(1) *m*-Nitrobenzoic acid

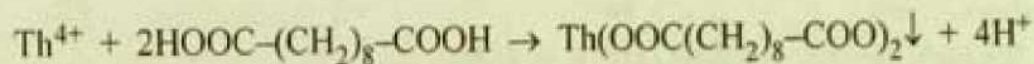
Reagent: Dissolve 1 g of *m*-nitrobenzoic acid in 250 ml of hot (~80°C) water, allow to cool overnight, filter and use the filtrate.

Th (IV) salts in neutral solution, on warming (~80°C) with an excess of *m*-nitrobenzoic acid (1) reagent form a white precipitate of Th-*m* nitrobenzoate (2) (distinction from cerium).



(2) Saturated solution of sebacic acid

Th (IV) salts react with saturated solution of sebacic acid, $\text{HOOC}-(\text{CH}_2)_8-\text{COOH}$, to produce a voluminous white precipitate of thoriumsebacate, $\text{Th}(\text{OOC}-(\text{CH}_2)_8\text{COO})_2$, (distinction from cerium).



8.7. Reactions of Vanadium (V^{IV} , V^{V})

Although vanadium compounds in several oxidation states (+2 to +5) are known, +5 state is most common and most stable oxidation state of vanadium. +2 state is strongly reducing.

Vanadium pentoxide, V_2O_5 , is the most commonly and commercially available compound of vanadium. It is slightly soluble in water, but readily dissolves in strong acids and alkalis, producing vanadates, which are analogons to phosphates. Vanadic acid, like phosphoric acid, can exist in ortho, meta- and pyro-forms (H_3VO_4 , HVO_3 and $\text{H}_4\text{V}_2\text{O}_7$ respectively), the only difference is that, for phosphoric acid, the ortho-form (H_3PO_4) is most stable, whereas, for vanadic acid, the meta-form (HVO_3) is most stable and the ortho-vanadates are least stable. NH_4VO_3 , NaVO_3 are commercially available.

Isopolyvanades are formed on acidification of aqueous solutions of vanadate salts. The compositions of the isopolyvanadates, of course, depend upon the concentrations of both vanadium (V) species and also of H^+ ion from the acid. Starting from simple ortho-vanadate (VO_3^-) ion, with rise of acidity, species like, $\text{VO}_3(\text{OH})^{2-}$, $\text{V}_3\text{O}_9^{3-}$, $\text{V}_{10}\text{O}_{28}^{6-}$, V_2O_5 and VO_2^+ are formed. Dioxovanadium (VO_2^+), i.e., vanadyl ion exists in strongly acidic solution.

Water soluble vanadyl sulfates, $\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ ($x = 2, 5$) are commercially available. Pyrovanadate ($\text{V}_2\text{O}_7^{4-}$) ion is stable in alkaline solution. It is, however, convenient to treat all these vanadate ions in terms of meta-vanadate (VO_3^-) ion. Tetravalent vanadium exists as the cationic species, VO^{2+} ion. V^{III} exists in aqueous solution mainly as VO^+ , $\text{V}(\text{OH})^{2+}$ ions. Hexaaquavanadium (III), $\text{V}(\text{H}_2\text{O})_6^{3+}$ ion exists in V^{III} alums, $\text{NH}_4\text{V}^{\text{III}}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. Divalent

vanadium compounds are strongly reducing, and air sensitive. $V^{II}SO_4 \cdot 7H_2O$ is isomorphous with its Cr^{II} and Fe^{II} analogues. $V(H_2O)_6^{2+}$ ion exists in *Tutton salts*, $M_2^I SO_4 \cdot V^{II} SO_4 \cdot 6H_2O$, where, M^I = alkali metal ion, NH_4^+ etc.

Indications

(1) Borax bead test

Oxidizing flame : Yellow when hot and greenish-yellow when cold (due to vanadates).

Reducing flame : Brownish when hot and emerald green when cold (due to V^{III} borate).

(2) Microcosmic salt bead test

Oxidizing flame: Yellow when hot and cold.

Reducing flame: Green when hot and cold.

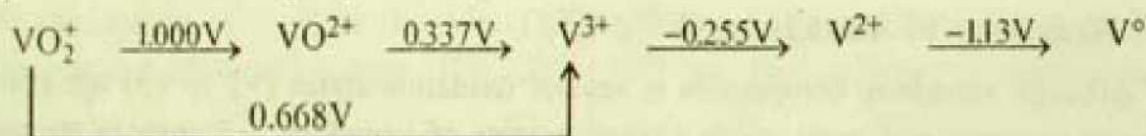
Redox Chemistry of Vanadium

Redox properties of different vanadium oxidation states are strongly dependent upon acidity of the solution. Tendency of oxo species formation increases with lowering of acidity, as will be evident from the Latimer diagrams of vanadium in (a) strongly acidic, (b) weakly acidic and (c) basic solutions:

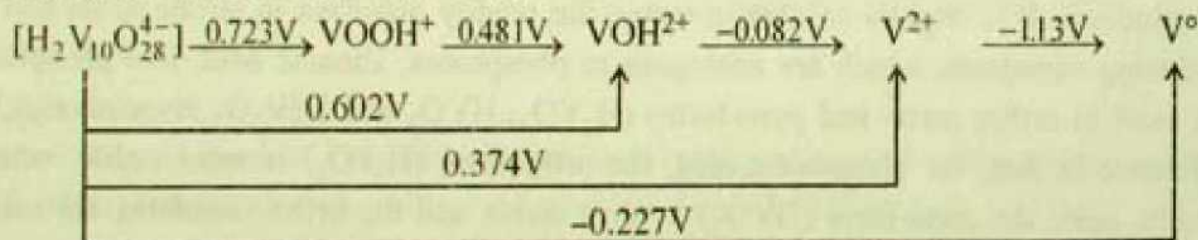
Oxidation

numbers +5 +4 +3 +2 0

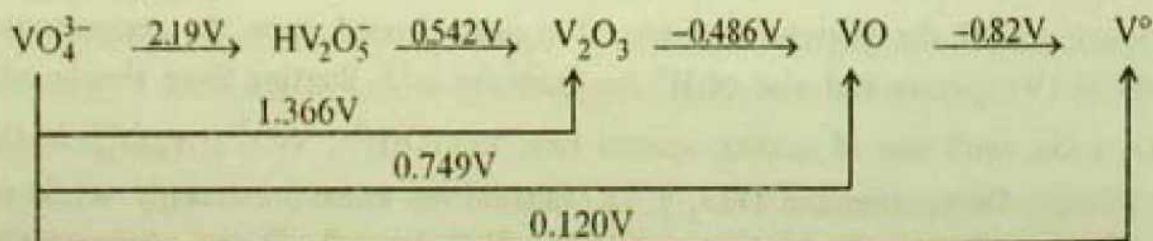
(a) Strongly acidic solution ($[H^+] = 1 M$)



(b) Weakly acidic solution (pH 3.0 ~ 3.5)



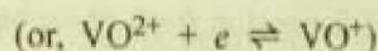
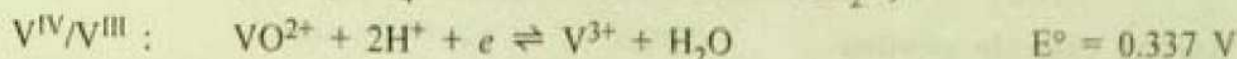
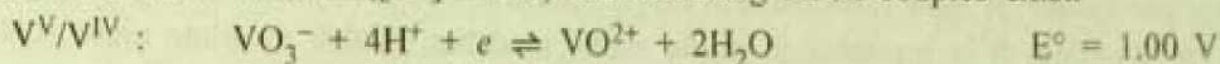
(c) Basic solution ($[OH] = 1M$)



Redox transformations of vanadium species are accompanied by interesting colour changes:

Oxidation states	+5	+4	+3	+2
Species ($[H^+] = 1M$)	VO_3^-	VO^{2+}	VO^+ (or, V^{3+})	V^{2+}
Colours	colourless-pale yellow	blue	green	violet

The half-reactions for the vanadium redox couples maybe formulated from its Latimer diagrams. In acid medium ($[H^+] = 1M$) the following redox couples exist:



It is evident from the half-reactions that the formal potentials of V^V/V^{IV} , V^{IV}/V^{III} and V^{III}/V^{II} couples are pH dependent. V^V is reduced to V^{IV} by moderate reducing agents, whereas, V^{II} is produced only when higher valent vanadium compounds are reduced by strong reducing agents. As for example:

(i) Reduction of vanadate (VO_3^-) to vanadyl (VO^{2+}) ion

In acidic solution, mild reducing agents, eg, H_2S , SO_2 , oxalic acid, Fe^{2+} , hydrazine, formic acid, ethanol reduce colourless (or pale-yellow) solution of vanadate (VO_3^-) ion to blue coloured vanadyl (VO^{2+}) ion. Reaction with H_2S takes place with separation of colloidal sulfur but vanadium sulfide is not precipitated:



All these reactions are slow in the cold, but takes place rapidly on warming.

(ii) Reduction of vanadate (VO_3^-) to vanadyl (VO^{2+}) to V^{3+} to V^{2+}

Strong reducing agents, eg, metallic zinc, cadmium, aluminium, Zn-amalgam in acid medium reduce colourless (or pale-yellow) vanadate (VO_3^-) ion first to blue vanadyl (VO^{2+}) ion, which is subsequently reduced to green V^{3+} ion and finally to violet V^{2+} ion.

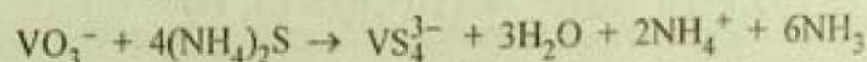
Reactions of Vanadate (VO_3^-) ion in solution

(1) Ammonium chloride

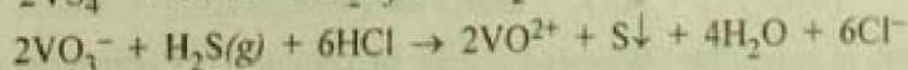
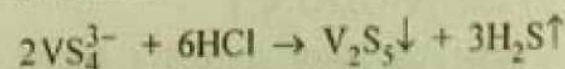
White precipitate of ammonium metavanadate (NH_4VO_3) crystallizes out on addition of solid ammonium chloride to vanadate solution. The precipitate is sparingly soluble in concentrated solution of NH_4Cl .

(2) Ammonium sulfide solution

Claret red colouration appears due to the formation of thiovanadate (probably VS_4^{3-}) ion:

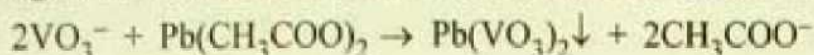


On acidification, brown precipitate of vanadium pentasulfide, V_2S_5 , appears with evolution of H_2S . The reaction is, however, incomplete, since the liberated H_2S reduces part of the unchanged vanadate to vanadyl (VO^{2+}) ion, giving a blue colour to the supernatant solution, with precipitation of sulfur.



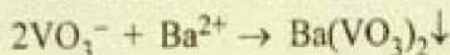
(3) Lead acetate solution

Yellow precipitate of lead vanadate, $\text{Pb}(\text{VO}_3)_2$ appears. The precipitate turns pale yellow to white on standing. It is insoluble in dilute acetic acid but soluble in dilute nitric acid.



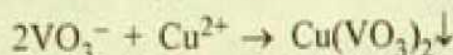
(4) Barium chloride solution

Yellow precipitate of barium vanadate appears, (distinction from phosphate and arsenate). The precipitate is soluble in dilute hydrochloric acid.



(5) Copper (II) sulfate solution

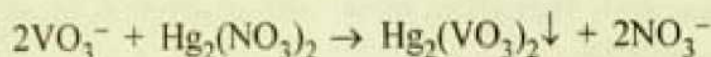
Green precipitate of $\text{Cu}(\text{II})$ metavanadate appears.



A yellow precipitate is formed with pyrovanadate ($\text{V}_2\text{O}_7^{4-}$).

(6) Mercurous nitrate, $\text{Hg}_2(\text{NO}_3)_2$ solution

$\text{Hg}(\text{I})$ nitrate reacts with neutral solution of vanadate to give white precipitate of $\text{Hg}(\text{I})$ vanadate:



(7) Ammonium molybdate + Ammonium nitrate + Conc. HNO_3

(Nitromolybdate reagent)

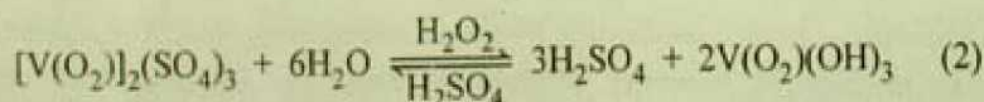
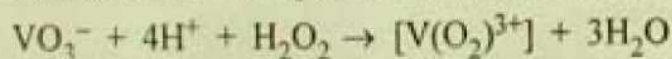
No precipitation with vanadate (distinction from phosphate and arsenate).

Note: If phosphate is present with vanadate, canary yellow precipitate of ammonium phosphomolybdate appears, with which vanadate is coprecipitated.

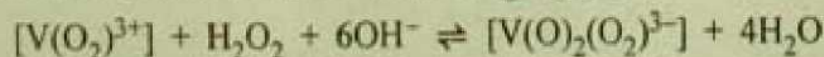
Confirmation

(1) Hydrogen peroxide test

In dilute sulfuric acid ($\sim 6-8N$) solution vanadate reacts with hydrogen peroxide to produce a blood-red to red-brown (i.e., wine-red) colouration due to the formation of peroxovanadium sulfate (1). Dilute solution of vanadate produces a pale-brown-pink colouration. In presence of excess of hydrogen peroxide, the wine-red coloured peroxovanadium sulfate (1) is transformed to yellow coloured orthoperoxovanadic acid (2).



The wine-red colour of the complex (1) also turns yellow on addition of alkali due to the formation of diperoxothrovanadate (V) ion, $[\text{V}(\text{O})_2(\text{O}_2)_2]^{3-}$.



The reaction is reversible. Wine-red colour of complex (1) reappears on acidification.



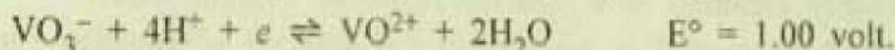
Mix a drop of the test solution and a drop of 8N H_2SO_4 . Wait for 2-3 minutes and add 1 drop of dilute 1% H_2O_2 solution. If necessary, add one more drop of H_2O_2 . A red to pink colour appears depending upon the amount of vanadium.

Limit of identification: 2.5γ of V

Limit of dilution : 1 : 20,000

(2) Tests based on reduction of Fe^{III} by V^{IV}

Redox potential of $\text{V}^{\text{V}}/\text{V}^{\text{IV}}$ couple is dependent upon pH (cf. p-138)



As a result, in acid medium vanadate (VO_3^-) ion can oxidize Fe^{II} to Fe^{III} ($E^\circ = 0.77$ volt).



or, simply, $\text{V}^{\text{V}} + \text{Fe}^{\text{II}} \rightleftharpoons \text{Fe}^{\text{III}} + \text{V}^{\text{IV}}$

But in neutral, or, alkaline medium Fe^{III} is reduced by vanadyl (VO^{2+}) ion to Fe^{II} .

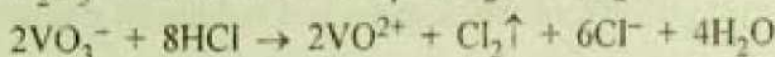
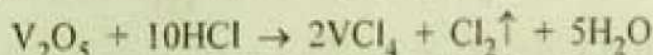
Fe^{II} produced in the alkaline medium may be detected by the appearance of (i) red colouration with 2,2'-bipyridine (bipy) in acid medium, or, (ii) red colouration with dimethylglyoxime in ammoniacal medium. Formation of brown precipitate of ferric hydroxide may be avoided by adding sodium dihydrogenphosphate NaH_2PO_4 , which in acid medium keeps Fe^{III} in solution in the form of colourless $[\text{Fe}(\text{HPO}_4)_2]^-$ complex ion, and in alkaline/ammoniacal medium, it forms light yellow precipitate of FePO_4 . NaK-tartrate or tartaric acid may also be used in place of NaH_2PO_4 .

Reagents: (i) Ferric chloride : 1% solution of $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ in dil.HCl

(ii) 2,2' - Bipyridine : 2% solution in 0.1 M HCl

(iii) Dimethylglyoxime : 1% solution in 95% ethanol.

Vanadium (V) is first reduced to V(IV) by digestion with conc -HCl.



The resulting vanadium (IV) is then treated with Fe^{III} solution, followed by the reagents (ii) or (iii).

Mix 1 drop of the test solution with 2 drops of conc.HCl on a small porcelain basin and evaporate to dryness in a **FUME CUPBOARD**. Allow to cool and add 1 drop of FeCl_3 solution in dil.HCl, 1 drop of sodium dihydrogenphosphate to mix thoroughly. Transfer the mixture to two adjacent cavities of a spot plate using a dropper and perform the following tests.

(i) To one of the cavities add 1-2 drops of 2,2'-bipyridine solution. A red colouration indicates Fe^{2+} , which is formed as FeCl_3 is reduced by V(IV)/ vanadyl (VO^{2+}) ion to Fe^{2+} ion.

Note: In stead of 2,2'-bipyridine, 2% solution of 1,10-phenanthroline in 0.1 M HCl may also be used.

Limit of identification : 0.1γ of V

Limit of dilution : 1: 5×10^5

(ii) Add 3-4 drops of dimethylglyoxime solution to the other cavity. Add a crystal of tartaric acid or Na-K-tartrate and drops of 1:1 aq-NH₃ until ammonical. Red colouration indicates Fe^{II}, arising from reduction of FeCl₃ by vanadium (IV) or, vanadyl (VO²⁺) ion.

Thus, this is an indirect test of vanadium.

Limit of identification : 1γ of V.

Limit of dilution: 1: 5 × 10⁴

(3) Tannin test

Reagent: Freshly prepared 50% solution of tannic acid in water.

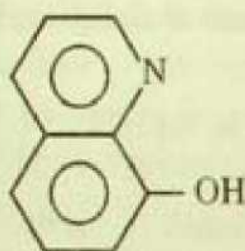
Place a drop of the neutral or acetic acid test solution of vanadate on a spot plate and add a few drops of 5% solution of tannic acid. An intense blue to blue-black colouration is produced if vanadate is present.

Add a small crystal of ammonium acetate. A dark blue to blue-black precipitate separates out.

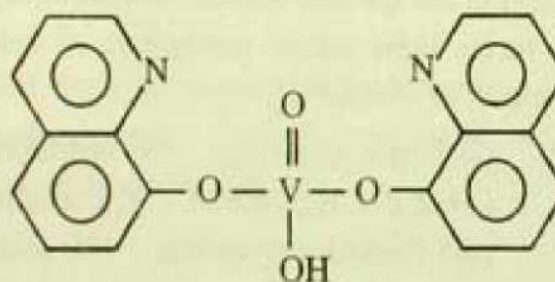
Add drops of dilute hydrochloric acid. The precipitate dissolves and the blue-black colour disappears.

(4) Test with 8-hydroxyquinoline (Oxine)

Vanadate ion forms a brown-black compound (2) with 8-hydroxyquinoline (oxine, 1) in acetic acid solution and also with molten oxine (m.p. 75°C).



(1)



(2)

Fe³⁺ and uranyl (UO₂²⁺) ions form black-green and red-brown oxinates respectively. In the detection of vanadium by oxine test, these metal ions should be absent. These ions can be rendered harmless by igniting a small portion of the sample to form oxides. If the oxide residue is extracted with ammonia, only vanadium oxide dissolves as vanadate, the other oxides remain undissolved.

Place a drop of the test solution, or, a pinch (<0.1 g) of the solid sample to be tested for vanadium in a small porcelain crucible and ignite it strongly. Cool to room temperature and add ~0.2 – 0.3 g of solid oxine and heat gently so that the temperature is raised to 250°C. A brown-black melt is formed if vanadium is present.

Limit of identification: 0.5γ of V.

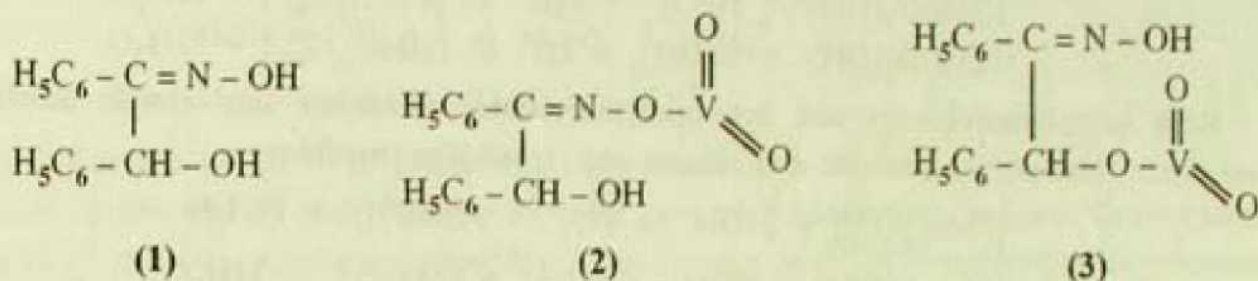
Limit of dilution : 1: 1×10⁴

Note: If molybdate, or, tungstate is present, the oxine melt should not be heated above 120°C, since the reagent may reduce Mo^{VI} and W^{VI} to their lower oxides, which are intensely coloured (*cf.* molybdenum blue, *cf.* Sect. 8.8).

(3) Test with α -benzoin oxime (Cupron)

Reagent: Saturated solution of α -benzoin oxime in ethanol.

In strongly acidic solution vanadate forms a yellow precipitate with α -benzoin oxime (1), due to anhydride formation between the OH group of the metallo acid with the NOH group (2) or with the C-OH group (3) of the reagent:



Molybdate and tungstate interfere, as they produce white precipitates of similar compositions as vanadate with the reagent. The yellow colour of the vanadate α -benzoin oxime complex can even be detected in presence of white precipitates of molybdate/tungstate complexes with the reagent, by digesting the mixture with water. Since the yellow coloured solution of the vanadium complex can be poured off and separated from the white precipitates due to molybdate and tungstate complexes. Coloured ions obscure the test. Interference due to Fe^{3+} ion maybe eliminated by complexing it by adding phosphoric acid.

Place a drop of the test solution on a spot plate, add 2 drops of α -benzoin oxime reagent and one drop of dilute 3N H_2SO_4 . A yellow precipitate, or, colouration appears if vanadate is present.

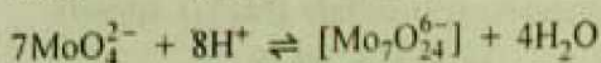
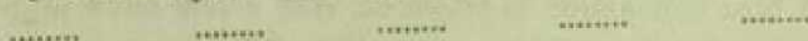
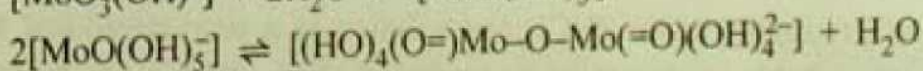
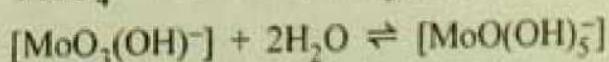
If Fe^{III} is present, add 1 drop of H_3PO_4 before addition of the reagent to mask the colour due to the iron-complex with the reagent.

Limit of identification : 1 γ of V

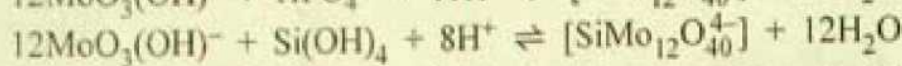
Limit of dilution : 1 : 5×10^4

8.8 Reactions Molybdenum (Mo^{VI} , Mo^{V} , Mo^{IV} , Mo^{III})

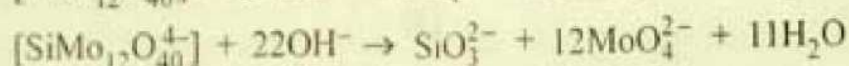
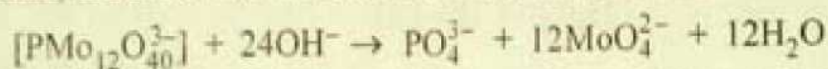
Most stable oxidation state of molybdenum is +6. Molybdate (MoO_4^{2-}) salts and molybdic acid, H_2MoO_4 (or, $\text{MoO}_3 \cdot x\text{H}_2\text{O}$) are the most stable compounds of molybdenum (VI), although molybdenum compounds in lower oxidation states, +5, +4, +3 and +2 are also known. Molybdic acid tend to polymerise in acid medium to form *isopoly molybdates*, of which heptamolybdate, ($[\text{Mo}_7\text{O}_{24}^{6-}]$) and octamolybdate, ($[\text{Mo}_8\text{O}_{26}^{4-}]$) are best known. For simplicity, molybdate (MoO_4^{2-}) ion is used in describing its reactions.



Such polymerisations in presence of phosphate, arsenate and silicate ions produce *heteropoly molybdates*, viz., phosphomolybdate, arsenomolybdate and silicomolybdate respectively. Most well known heteropolyanions of analytical importance are the 1:12 heteropolymetallates, $[X^{n+}M_{12}^{VI}O_{40}]$, where, $X^{n+} = P^V, As^V$ and Si^{IV} ; $M = Mo^{VI}$ and W^{VI} .



Both isopolymolybdates and heteropolymolybdates dissociate into simple anions, eg. molybdate, phosphate, arsenate and silicate etc. in alkaline medium:



Commonly available molybdenum compounds include : MoO_3 , $M_2^I MoO_4$ ($M^I = Na^+, NH_4^+$), $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, $(NH_4)_4Mo_8O_{26} \cdot 5H_2O$, $H_3[PMo_{12}O_{40}]$, $(NH_4)_3[PMo_{12}O_{40}]$, $(NH_4)_3[AsMo_{12}O_{40}]$ etc.

Indication

(1) Microcosmic salt bead test

Oxidizing flame: Yellow to green when hot and colourless when cold.

Reducing flame: Brown when hot and green when cold.

(2) Borax bead test

Oxidizing flame: Yellow when hot and colourless when cold,

Reducing flame: Brown when hot and cold.

(3) Hot concentrated sulfuric acid

Place a grain (<0.1 g) of the solid sample in a small porcelain dish or, a crucible, add 1 drop of conc. H_2SO_4 and evaporate by gentle heating inside a **FUME CUPBOARD**. A blue mass results due to the formation of 'molybdenum blue'. The blue colour is discharged on dilution with water.

Note: Mo^{VI} is partly transformed to molybdenum blue, which consists of Mo_4O_{11} ($\equiv Mo_2O_5 \cdot 2MoO_3$).

Reactions of Molybdate ion in solution

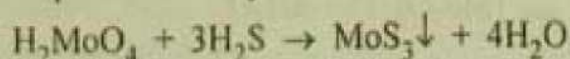
(1) Dilute hydrochloric acid

To a drop of the concentrated test solution on a spot plate add a drop of dil. (1:1) HCl. Yellow to white precipitate of molybdic acid ($H_2MoO_4 \equiv MoO_3 \cdot H_2O$) appears.



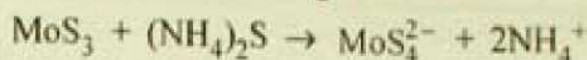
(2) H_2S - water

Take 1 ml of slightly acidic (HCl) test solution in a semi-micro test tube, add 1 drop of dilute H_2S -water. A blue colouration is produced. Add a few more drops of saturated H_2S -water. A brown precipitate of molybdenum trisulfide (MoS_3) appears.



Note: Blue colouration may be due to reduction of Mo(VI) to lower oxidation state (*cf.* molybdenum blue).

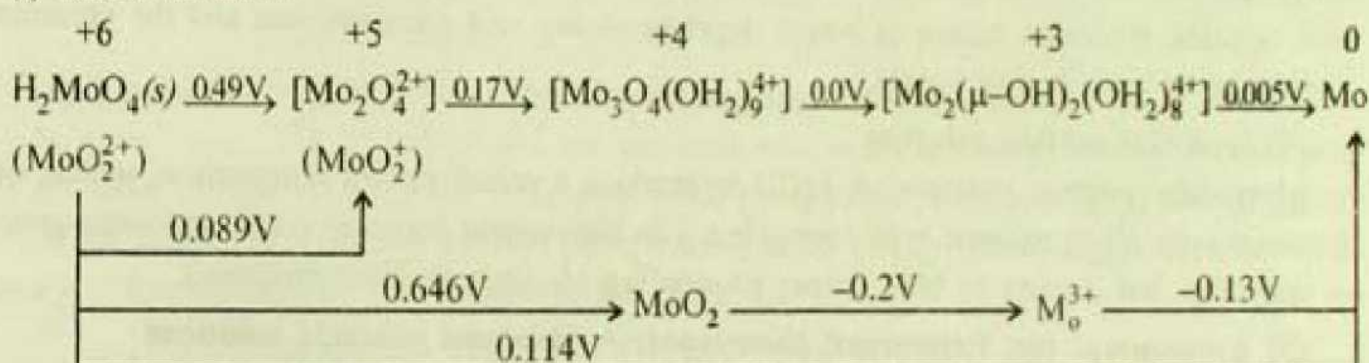
The brown precipitate of MoS_3 dissolves in ammonium sulfide to produce a brown solution containing tetrathiomolybdate (MoS_4^{2-}) ion. The precipitate of MoS_3 reappears with evolution of H_2S on acidification of the resulting solution.



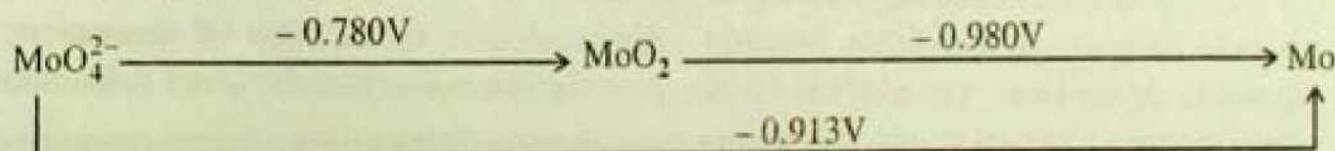
(3) Reduction of Mo^{VI} to lower oxidation states

Redox potentials of molybdenum couples are of intermediate values. Consequently varieties of reducing agents including Mo^{III} can convert Mo^{VI} to lower valent molybdenum compounds, particularly to colloidal *molybdenum blue*, which maybe formulated as Mo_4O_{11} ($\equiv \text{Mo}_2\text{O}_5 \cdot 2\text{MoO}_3$), or, $\text{Mo}_8\text{O}_{23} \cdot x\text{H}_2\text{O}$ ($\equiv \text{Mo}_2\text{O}_5 \cdot 6\text{MoO}_3 \cdot x\text{H}_2\text{O}$) etc. The important molybdenum redox couples of relevance to aqueous solutions maybe derived from the Latimer diagrams of molybdenum in (i) acidic and (ii) basic solutions.

(i) Acidic solution

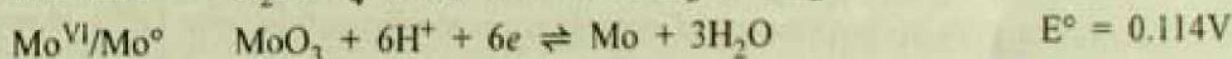
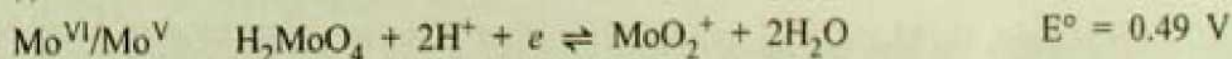


(ii) Basic solution

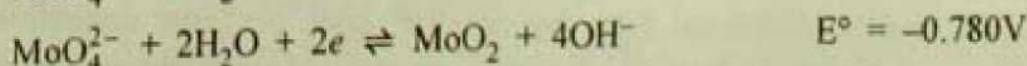
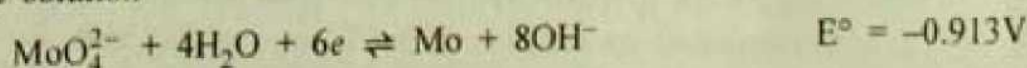


The half-reactions for some important molybdenum redox couples, as derived from the above diagrams are the following:

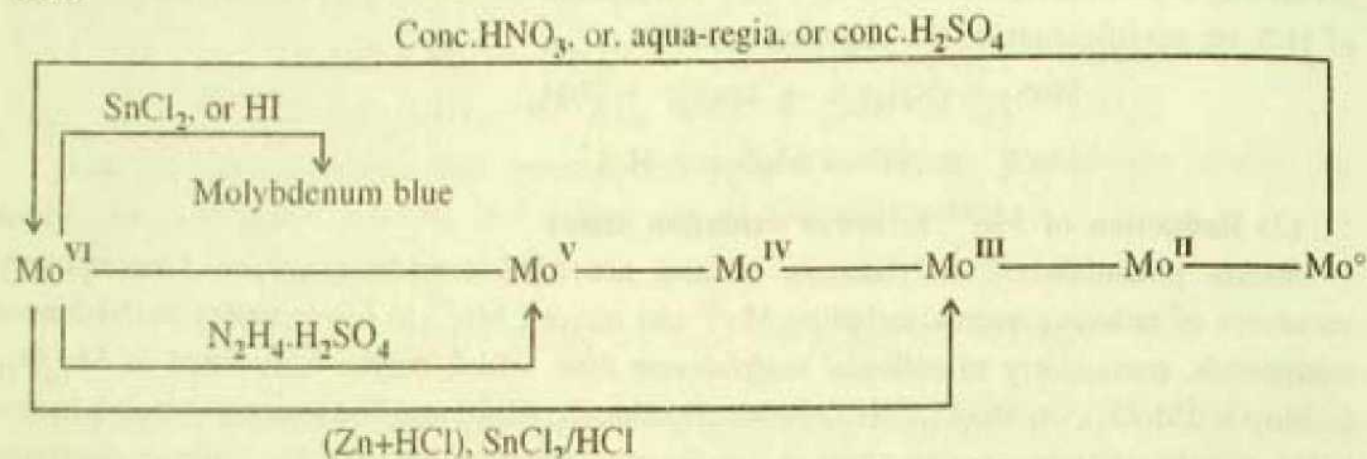
(i) In acidic solution



(ii) In alkaline solution



Since E° values of most of the molybdenum redox couples are modest and their formal potentials vary with acidity of the solutions, molybdates can be reduced by varieties of reducing agents to lower valent molybdenum species, which may be identified by their characteristic tests.



Reducing agents such as, Zn/HCl, SnCl₂ in dilute hydrochloric acid medium, reduce molybdate ion first to *molybdenum blue* and then to a green and finally to a brown coloured Mo^{III} species, the exact nature of which depends on the acid concentration and the presence or absence of complexing agents.

(4) Iron (II) sulfate solution

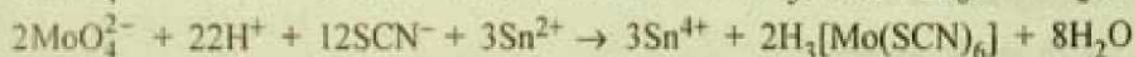
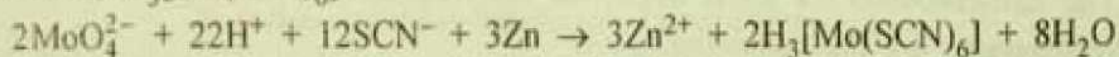
Molybdate solution reacts with Fe(II) to produce a redish brown colouration, which, on treatment with dilute mineral acid, turns blue. The blue colour becomes paler, and more green on warming, but returns to blue colour on cooling (distinction from tungsten).

(5) Ammonium (or, Potassium) thiocyanate + Stannous chloride solutions

Reagents: (i) 10% NH_4SCN (or KSCN) in water.

(ii) 5% Stannous chloride in 3M HCl.

Acid solution of molybdate becomes yellow coloured on addition of ammonium, or, potassium thiocyanate. On addition of zinc dust, or, stannous chloride, a red colouration is produced, as MoO_4^{2-} is reduced to Mo^{III} , which forms soluble hexathiocyanatomolybdate (III) complex acid, $\text{H}_3[\text{Mo}(\text{SCN})_6]$.



The complex acid, $\text{H}_3[\text{Mo}(\text{SCN})_6]$, is soluble in ether. The red colouration of $\text{Mo}^{\text{III}}\text{-SCN}^-$ complex is produced even in the presence of phosphoric acid (distinction from Fe^{III}). However, as molybdate reacts with phosphate in acidic solution to produce phosphomolybdate, of which the ammonium salt, $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]$, forms a canary yellow precipitate, molybdate should be reduced to Mo^{III} by SnCl_2/HCl or Zn/HCl before the addition of thiocyanate. Interference due to Fe^{III} is also eliminated on addition of SnCl_2 , or, metallic zinc. Fe^{III} is reduced to Fe^{II} by SnCl_2 and to elemental form by zinc. Fe^{II} does not give colouration with thiocyanate. Sensitivity of the test is, however, lower in presence of much phosphate, oxalate and tartarate.

Mercury (II) interferes by consuming thiocyanate in the form of mercuriothiocyanate complex, $[\text{Hg}(\text{SCN})_4]^{2-}$ ion. Nitrite ion, if present, forms soluble nitrosyl thiocyanate, NOSCN . Tungstate interferes by forming blue insoluble lower oxides. However, interference due to tungsten may be eliminated by capillary separation technique on a filter paper. Ti, V, U salts do not interfere.

Procedure

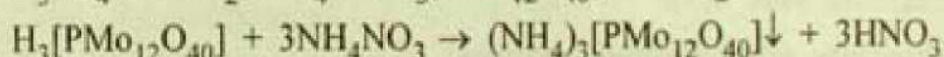
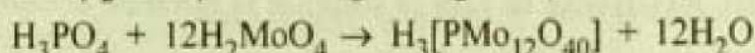
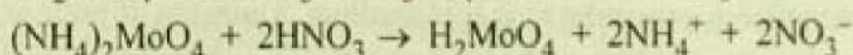
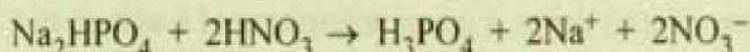
Place a drop of the acidic (HCl) test solution on a Whatman No. 1 filter paper strip previously moistened with 1:1 hydrochloric acid. Allow the paper to dry. Now add a drop of 10% solution of NH_4SCN (or KSCN) using a capillary tube. An intense red fleck is formed if Fe^{III} is present. Now using a capillary dropper add 1 drop of SnCl_2 solution on the red fleck. SnCl_2 reduces Fe^{III} to Fe^{II} and the red fleck due to $\text{Fe}^{\text{III}}\text{-SCN}^-$ complex disappears, but simultaneously a brick red fleck due to $\text{Mo}^{\text{III}}\text{-SCN}^-$ complex appears and moves toward the periphery of the paper if molybdenum is present, as SnCl_2 reduces MoO_4^{2-} to Mo(III) . If tungstate is present, it is also reduced by SnCl_2 to a blue precipitate of W_2O_5 . Now using a capillary dropper, hold a solution of (1:1) HCl upon the spot. The brick-red coloured ring of $\text{H}_3[\text{Mo}(\text{SCN})_6]$ complex moves out leaving a blue spot of W_2O_5 at the centre.

Limit of identification: 0.1 γ of Mo

Limit of dilution: 1: 5×10^5

(6) Phosphoric acid (or, Disodium hydrogenphosphate) solution

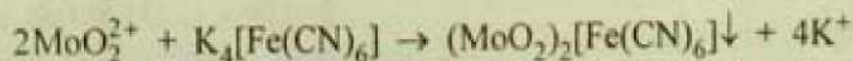
In nitric acid medium, molybdate ion (or, molybdic acid) combines with phosphate ion (or phosphoric acid) to form the heteropoly acid, phosphomolybdic acid, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, of which the ammonium salt, ammonium phosphomolybdate, $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]$, separates as a canary yellow precipitate (*cf.* phosphate test Sect. 5.19).



The canary yellow precipitate of ammonium phosphomolybdate is formed in slightly warm solution (boiling is not required, distinction from arsenomolybdate). The precipitate is insoluble in tartaric acid (distinction from arsenomolybdate), but soluble in alkali, forming simple molybdate and phosphate ions (similarity to arsenomolybdate) (*cf.* Sect. 4.8)

(7) Potassium ferrocyanide solution

Redish brown precipitate of molybdenyl ferrocyanide appears on addition of potassium ferrocyanide solution to a molybdate solution in acid medium. The precipitate is readily soluble in dil. NaOH solution and in *aq*- NH_3 solution (difference from copper(II) and uranyl ferrocyanides).



(8) Stannous chloride + 2,2'-bipyridine reagent

Reagent: (i) 0.01g of 2,2'-bipyridine in 0.5 ml of 0.1 M HCl

(ii) 5% solution of stannous chloride in 3M.HCl.

Place a drop of the (dilute HCl) acidic solution of molybdate on a drop reaction paper and add a drop of 2,2'-bipyridine (bipy) reagent. Allow the spot to dry. Now add a drop of SnCl_2 solution on the spot. A red colouration appears.

In HCl medium SnCl_2 reduces molybdate to MoCl_3 , which forms a soluble red coloured complex, $[\text{Mo}(\text{bipy})_3]^{3+}$ ion with 2,2'-bipyridine.

Limit of identification : 0.4γ of Mo.

(9) Diphenylcarbazide reagent

Reagent: 0.2% solution of diphenylcarbazide in 10% acetic acid.

Place a drop of the weakly acidic solution of molybdate on a drop reaction paper and add a drop of diphenylcarbazide reagent. A violet colouration appears.

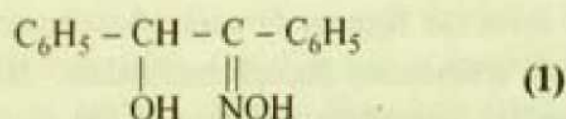
The exact chemistry of this reaction is obscure. Possibly diphenylcarbazide is oxidized to diphenylcarbazone by molybdate and this is followed by complex formation of diphenylcarbazide or diphenylcarbozone or both with molybdenum species or molybdate (*cf.* chromate test Sect. 5.18).

Limit of identification: 0.3γ of Mo.

(10) α-Benzoinoxime (or, Cupron reagent)

Reagent: 5% solution of α-benzoin oxime in 95% ethanol.

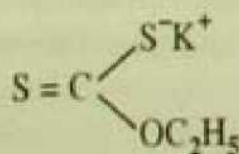
α-Benzoin oxime (H_2Bx , 1) in dilute sulfuric acid medium quantitatively precipitates molybdate as a white precipitate of composition, $\text{MoO}_2(\text{Bx})$,



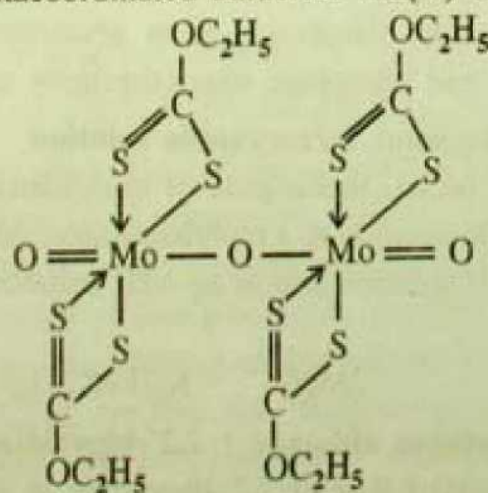
In ammoniacal medium $\text{Cu}(\text{II})$ forms a green precipitate of $\text{Cu}(\text{Bx})$, but it does not interfere with molybdenum, which is precipitated in acid medium. Tungsten, if present, is also precipitated with molybdenum. $\text{Fe}(\text{III})$, $\text{Al}(\text{III})$ may be kept in solution as tartarate complexes. (*cf.* vanadium tests for reactions Sect. 8.7).

(11) Potassium ethylxanthate reagent

Acidic (HCl) solution of molybdate reacts with potassium ethylxanthate (1) to give a red-purple colouration due to the formation of a hexacoordinated dinuclear $\text{Mo}(\text{V})$ complex (2).



(1)



(2)

With large amount of molybdenum, the compound separates as dark oily drops.

Place a drop of the slightly acidic test solution on a spot plate and add a small crystal of potassium ethylxanthate and 2 drops of dilute ($\sim 2M$) HCl. An intense red-violet colouration appears.

This test is specific for molybdenum if fluoride and phosphate are absent.

Limit of identification: 0.04 γ of Mo

Limit of dilution: 1 : 2.5×10^5

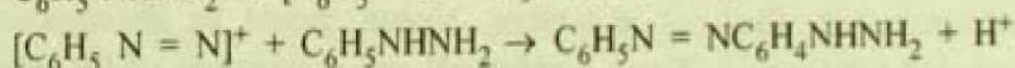
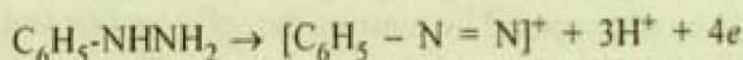
Alternatively, impregnate a Whatman No. 1 filter paper strip with $ZnSO_4$ or $CdSO_4$ solution and allow the paper to dry. Now immerse the paper in an aqueous solution of potassium ethyl xanthate and dry the paper. $Zn(II)$, or, $Cd(II)$ xanthate is formed on the filter paper. Wash the paper with water and dry. Now add a drop of the test solution followed by 2 drops of dilute HCl solution ($\sim 2M$). A red fleck or a red ring appears.

Limit of identification: 0.01 γ of Mo

(12) Phenylhydrazine reagent

Reagent: Mix phenylhydrazine and glacial acetic acid in 1:2 proportion.

Acid solution of molybdate reacts with phenylhydrazine giving a pink to red colouration, or a, red precipitate depending upon the quantity of molybdenum present. Possibly molybdate oxidizes phenylhydrazine to the corresponding diazonium compound which couples with the excess phenylhydrazine and also forms complex with molybdenum species to give the red colouration.



Procedure

(i) Mix a drop of the test solution and a drop of the reagent on a spot plate. Depending upon the amount of molybdenum present, a more or less deep red colouration appears.

Limit of identification : 0.32 γ of Mo

Limit of dilution: 1 : 1.5×10^5

(ii) Place a drop of the reagent on a drop reaction paper and before it has soaked in the paper, add a drop of the test solution. After a few minutes a red ring is formed around the spot.

Limit of identification : 0.13 γ of Mo

Limit of dilution: 1: 3.2×10^5

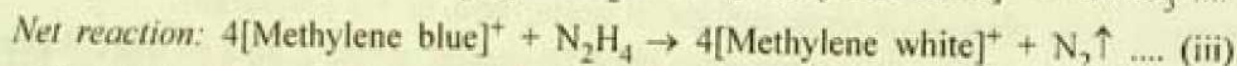
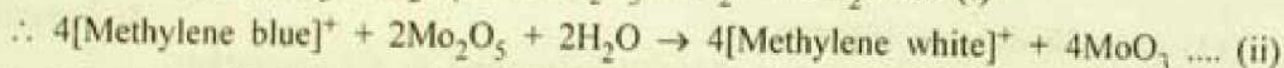
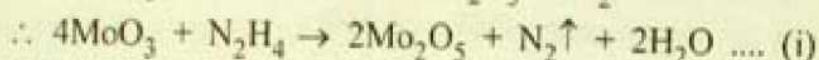
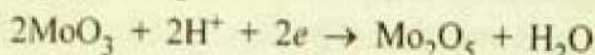
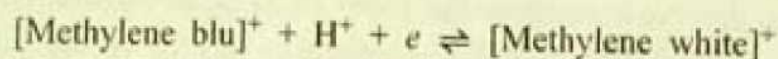
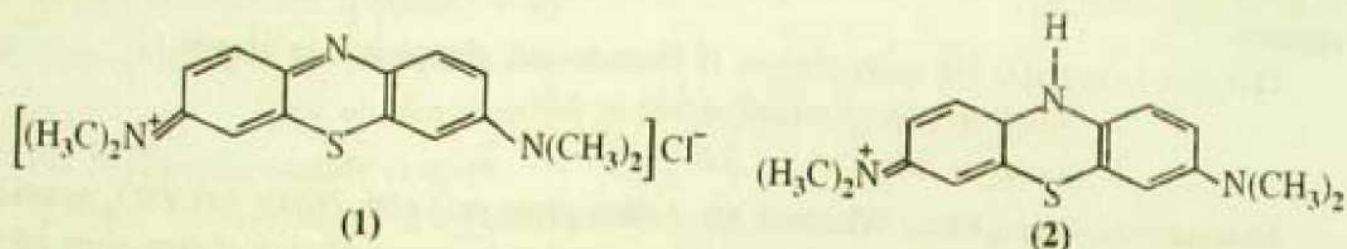
(13) Catalysis of reduction of methylene blue by hydrazine

Reagent: (i) $1.2 \times 10^{-3}\%$ aqueous solution of methylene blue.

(ii) Hydrazine sulfate (solid).

Methylene blue cation (1) is not reduced by hydrazine sulfate ($N_2H_4 \cdot H_2SO_4$) solution even at the boiling temperature. But in the presence of traces of molybdate, the reduction of methylene blue cation (1) to the leuco compound, methylene white cation (2), takes place rapidly. Mo^{VI} (molybdate) is rapidly reduced to Mo^V by hydrazine sulfate (i) in acid solution on warming. The Mo^V in its turn reduces (1) to (2) and it self is reoxidized to Mo^{VI} (ii), which is again

reduced by hydrazine and so on. Thus, it is an intermediate reaction catalysis, involving Mo^{VI} and Mo^{V} , although molybdenum does not appear in the net chemical equation (iii), of the reaction.



U^{VI} , W^{VI} , Cr^{VI} , Cr^{III} , V^{V} , V^{IV} , Fe^{II} , Cu^{II} , Co^{II} , Ni^{II} salts do not interfere. Decolourization of the dye is difficult to recognise in presence of coloured ions. W_2O_5 reduces methylene blue slowly. Tungstate, if present, may be masked as its fluoro complex, $[\text{WO}_3\text{F}_2]^{2-}$ ion, by adding alkali fluoride, to prevent the formation of blue W_2O_5 due to reduction of $\text{W}(\text{VI})$ by N_2H_4 . Sulfide, if present, should be decomposed by roasting the solid sample and molybdenum should be extracted with alkali as molybdate. Nitrate should be decomposed by fuming with concentrated formic acid (**Fume Cupboard**) and evaporation of the ignition residue before addition of N_2H_4 , which may be oxidized by nitric acid.

In two semi-micro test tubes, mix four drops of 0.0012% aqueous solution of methylene blue with a few grains (~20-30 mg) of hydrazine sulfate. To one of the test tubes, add one drop of the weakly acidic test solution and to the other test tube, add equal volume of water in place of sample solution. Place both the test tubes on a hot water bath (Fig. 3.15). In the test tube containing the molybdate sample, the colour of methylene blue is discharged within 2-3 minutes, whereas, the blank remains unchanged.

Limit of identification: 0.012% of Mo .

Limit of dilution: 1 : 4.16×10^6

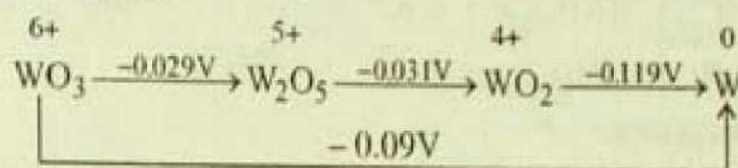
Confirmation

- (1) $\text{NH}_4\text{SCN}/\text{KSCN}$ test
- (2) SnCl_2 - 2,2'-bipyridine test
- (3) Potassium ethylxanthate test.
- (4) Catalysis of methylene blue reduction by hydrazine test.

8.9. Reactions of Tungsten (W^{V} & W^{VI})

Tungsten is a member of the same periodic group (Group-16) as molybdenum, and naturally it is chemically quite similar to molybdenum. Tungsten, like molybdenum, forms compounds

in a number of oxidation states ranging from +6 up to +2, of which +6 is the most stable state, +5 state is also stable, +4 state is unstable, but may be stabilized as fluoro and oxalato complexes. +3 and +2 states are strongly reducing, as is evident from its Latimer diagram for acidic solution. Interconversion among the different oxidation states of tungsten is possible using appropriate redox reagent.



Tungstic acid, WO_3 is a bright yellow solid, sparingly soluble water, but soluble in alkali and ammonia, due to the formation of tungstates of variable compositions. Alkali tungstates, on acidification, precipitate orthotungstic acid, $\text{WO}_3 \cdot \text{H}_2\text{O}$ ($\equiv \text{H}_2\text{WO}_4$). Tartarate, citrate and oxalate inhibit the precipitation of tungstic acid due to complex formation. Like molybdenum, tungsten also forms *isopoly*-and *heteropoly*-anions. The most well characterised isopoly and heteropoly tungstates are : $[\text{H}_2\text{W}_6\text{O}_{22}]^{6-}$, $[\text{W}_7\text{O}_{24}]^{6-}$, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{10-}$; $[\text{XW}_{12}\text{O}_{40}]^{3-}$ ($\text{X} = \text{P}, \text{As}$), $[\text{XW}_{12}\text{O}_{40}]^{4-}$ ($\text{X} = \text{Si}, \text{Ge}$), $[\text{X}_2\text{W}_{18}\text{O}_{62}]^{6-}$ ($\text{X} = \text{P}, \text{As}$).

It forms heteropoly anions with phosphoric acid, silicic acid and boric acid. Silicotungstic acid, $\text{H}_4[\text{SiW}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$, is a reagent for alkaloids. Other commonly available tungsten compounds include: $\text{WO}_3 \cdot x\text{H}_2\text{O}$, $\text{H}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $\text{H}_3[\text{PW}_{12}\text{O}_{40}] \cdot x\text{H}_2\text{O}$, etc.

Indication

(1) Microcosmic salt bead test

Oxidizing flame: Pale yellow when hot, colourless when cold.

Reducing flame: Green when hot, blue when cold. The colour of the bead changes to blood red upon addition of a small amount of ferrous sulfate.

(2) Borax bead test

Oxidizing flame: Yellow when hot, colourless when cold.

Reducing flame: Yellow when hot, yellowish brown when cold.

Reactions of Tungstate (WO_4^{2-}) ion in solution

Reactions involving precipitation of tungstates/tungstic acid

(1) Dilute hydrochloric acid

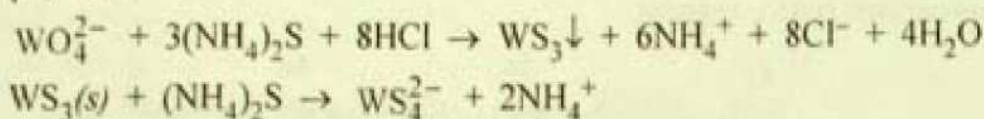
To 1 drop of alkali tungstate solution in a semi-micro test tube add a few drops of (1:1) dil.HCl. White precipitate of hydrated orthotungstic acid, $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$ appears in the cold. Boil the mixture, the colour of the precipitate changes to yellow (H_2WO_4). The precipitate is insoluble in dilute HNO_3 , dil. H_2SO_4 , but not in dil. H_3PO_4 (possibly due to the formation of phosphotungstic acid that precipitates). Tartarate, oxalate, citrate etc., inhibit the precipitation of tungstic acid. It is soluble in ammonia (distinction from silicic acid, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$).

(2) H_2S -water

No precipitation in acid medium.

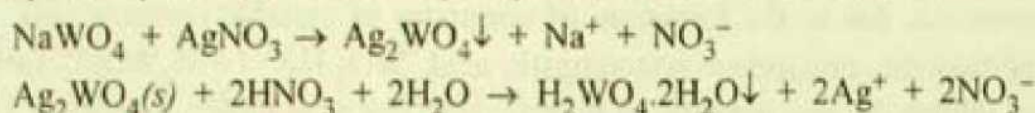
(3) Ammonium sulphide solution

No precipitation in ammoniacal medium. On acidification with dil.HCl, a brown precipitate (WS_3) appears. The precipitate dissolves in excess of ammonium sulfide solution forming tetra thiotungstate (WS_4^{2-}) ion:



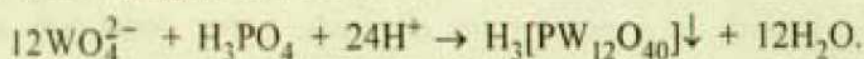
(4) Silver nitrate solution

A pale yellow precipitate of silver tungstate is formed. The precipitate is soluble in ammonia solution, but decomposed by nitric acid, due to precipitation of white, hydrated tungstic acid.



(5) Phosphoric acid

To 1 ml of the acidic (HNO_3) test solution add 1-2 drops of phosphoric acid and warm slightly. White precipitate of phosphotungstic acid (or, dodecatungstatophosphoric acid), $H_3[PW_{12}O_{40}]$, or, $H_3[P(W_3O_{10})_4]$, appears.



The precipitate is soluble in excess of the reagent and also in alkali.

Reactions involving reduction of W(VI)

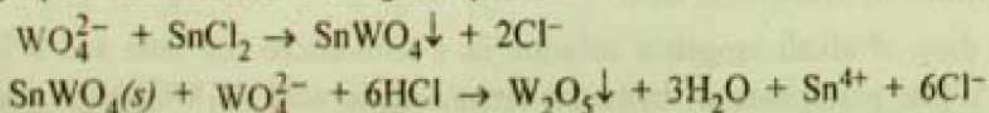
(1) Zn-Hydrochloric acid

Place a drop of the test solution or a grain of the solid sample on a spot plate, mix with a drop of HCl. Add a minute amount of Zn-dust and stir with a glass rod. A blue colouration or a precipitate appears, as W(VI) is reduced to W_2O_5 (tungsten blue):



(2) Stannous chloride solution

Place a drop of the neutral or weakly acidic (HCl) test solution on a small porcelain crucible, add 1-2 drops of $SnCl_2$ solution. Initially a yellow precipitate (possibly of $SnWO_4$) appears. Add 1 drop of HCl and warm slightly. A blue colouration or a blue precipitate (due to W_2O_5) appears depending upon the amount of tungsten present.



Molybdenum gives similar reaction with $SnCl_2$. Tungsten and molybdenum may be differentiated by $SnCl_2$ -thiocyanate-HCl test described below.

Confirmation

(1) $SnCl_2$ - NH_4SCN -HCl test (distinction between W and Mo)

In presence of hydrochloric acid, $SnCl_2$ reduces both tungstate and molybdate to blue coloured W_2O_5 and Mo_2O_5 respectively. If, however, thiocyanate is present, molybdate is further

reduced to Mo^{III} species, $\text{H}_3[\text{Mo}(\text{SCN})_6]$, which forms a red colouration. If the test is conducted on a filter paper strip, the red coloured Mo^{III} complex diffuses out by capillary action leaving a blue coloured central spot due to W_2O_5 .

Place a drop of conc. HCl on a Whatman No. 1 filter paper strip and add a drop of the test solution at the centre of the spot. If tungstate is present a yellow stain appears. Add 1 drop of 10% NH_4SCN (or KSCN) solution and then a drop of stannous chloride solution using capillary droppers. An intense red spot due to $\text{H}_3[\text{Mo}(\text{SCN})_6]$ appears if molybdenum is present. Now using a capillary dropper, hold a solution of (1:1) HCl upon the red spot. The red spot gradually moves out or disappears leaving a blue spot due to tungsten blue.

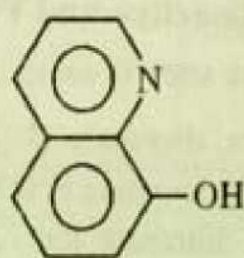
Limit of identification: 4 γ of W.

Limit of dilution: 1 : 12,500.

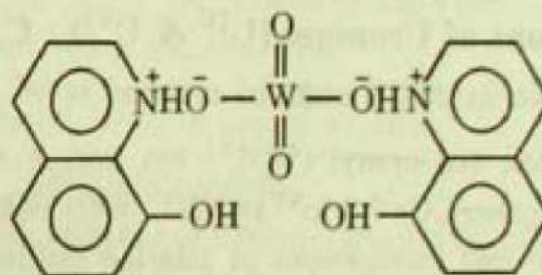
(2) Test with 8-hydroxyquinoline (Oxine)

Reagent: 5% solution of oxine in ethanol.

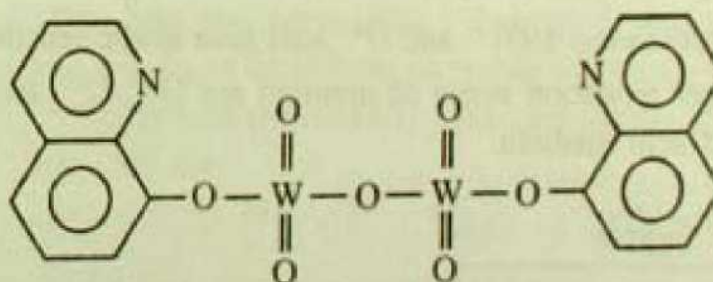
When concentrated solution of alkali tungstate (WO_4^{2-}) is treated with oxine (1) solution in conc. HCl , a white precipitate of tungstic acid $\text{WO}_3 \cdot x\text{H}_2\text{O}$ appears. But if a neutral, or, an acetic acid solution of tungstate is treated with an alcoholic solution of oxine, an orange-yellow precipitate of oxinium tungstate (2) appears, which is not decomposed by conc. HCl , but transformed to red-brown oxine ester of pyrotungstic acid (3). Such conversion of (2) to (3) forms the basis of detection of small quantities of tungsten.



(1)



(2)



(3)

Place a drop of neutral, or, acetic acid, or, weakly alkaline test solution on a spot plate and add 1 drop of 5% alcoholic solution of oxine followed by 1-2 drops of conc. HCl . A brown precipitate or colouration appears depending upon the amount of tungsten present.

Limit of identification : 15 γ of W

Limit of dilution: 1 : 33,333

(3) $\text{KHSO}_4\text{-H}_2\text{SO}_4$ - Phenol test (*Defacqz Reaction*)

When a tungstate salt in solid state is fused with KHSO_4 and the melt after cooling, is extracted with conc. H_2SO_4 and treated with a little phenol, a red colouration is produced (distinction from molybdenum). If instead of phenol, hydroquinone is used, a redish violet colouration is produced.

Take a grain of the solid sample (or, the residue obtained after evaporating a few drops of the test solution to dryness) on a porcelain crucible and mix it with ~4-5 times of its bulk of KHSO_4 . Heat the mixture gently to fusion inside a **FUME CUPBOARD** and maintain the temperature until a clear melt is formed. Cool the melt, add 1-2 drops of conc. H_2SO_4 and mix with a glass rod. Add a small amount of phenol and a few more drops of conc. H_2SO_4 . An intense red colouration is produced if tungsten is present.

Limit of identification: 2γ of W.

(4) Test with Fe(II) sulfate solution

Reagent: 0.5 M solution of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or of Mohr's salt in ~0.1 M H_2SO_4 .

Take 1-2 drops of the neutral, or, weakly acidic test solution in a semi-micro test tube, add 1-2 drops of Fe(II) sulfate solution. A brown precipitate is formed. Add a few drops of dil. HCl, the precipitate turns white. Heat the mixture gently. The colour changes to yellow, (distinction from the precipitate formed with molybdate which turns blue on treatment with acids).

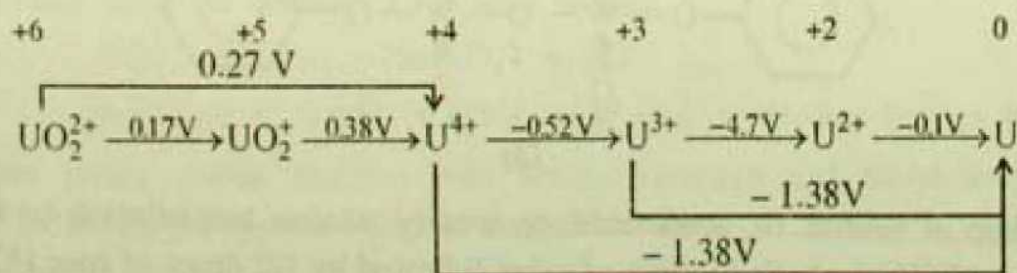
8.10. Reactions of Uranium (U^{IV} & U^{VI}) : CAUTION: Radioactive and Poisonous

Most stable oxidation state of uranium is +6. In this oxidation state it exists both as a cationic species, viz. uranyl (UO_2^{2+}) ion, and as an anionic species, diuranate ($\text{U}_2\text{O}_7^{2-}$) ion. Unlike its congeners, Cr^{VI} , Mo^{VI} and W^{VI} , for which isopoly anions predominate in acid medium and dissociate into monoanions in alkaline medium, formation of diuranate ion is favoured in alkaline medium, and in acid medium it is transformed to uranyl cation:

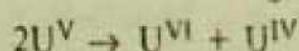


Aqueous solutions containing UO_2^{2+} and U^{4+} ions give acidic reactions due to hydrolysis.

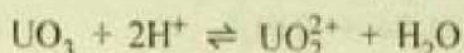
Apart from U^{VI} , other oxidation states of uranium are U^{III} , U^{IV} and U^{V} , as shown in its Latimer diagram in 1M acid medium.



While U^{III} and U^{IV} are reducing, U^{V} readily disproportionate to U^{IV} and U^{VI} :



Green coloured U_3O_8 is essentially a mixed valence oxide, $U^{IV}O(U_2^{VI}O_7)$ or, $U^{IV}(U^{VI}O_4)_2$. UO_3 is a red brown coloured amphoteric oxide. It reacts with acids to give uranyl (UO_2^{2+}) salts and with alkali it forms uranate (UO_4^{2-}) and diuranate ($U_2O_7^{2-}$) ions:



Uranyl nitrate hexahydrate, $UO_2(NO_3)_2 \cdot 6H_2O$ is a *triboluminescent* solid (emission of light on friction or grinding), soluble in water, alcohol and in ether. Uranyl sulfide, phosphate and ferrocyanide are sparingly soluble. Uranyl chloride, UO_2Cl_2 , alkali metal and ammonium diuranates, e.g. $Na_2U_2O_7$, $(NH_4)_2U_2O_7$ respectively, are yellow solids. U^{IV} compounds are green and uranyl (U^{VI}) compounds are yellow.

Indication

(1) Borax bead test

Oxidizing flame: Yellow when hot, pale-yellow when cold.

Reducing flame: Green when hot, bottle-green when cold.

(2) Microcosmic salt bead test

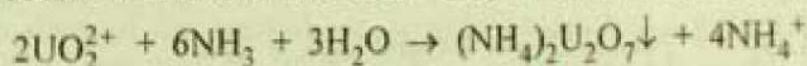
Oxidizing flame: Yellow when hot, yellow-green when cold.

Reducing flame: Green when hot and cold.

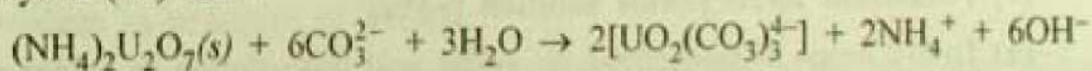
Reactions of Uranyl (UO_2^{2+}) ion in solution

1. Aqueous-ammonia-Ammonium carbonate reagent

Take a drop of the test solution in a semi-micro test tube and add a drop of *aq-NH₃* solution. Yellow precipitate of ammonium diuranate is formed, which is insoluble in excess of the reagent:



Divide the precipitate into two parts. Add 1-2 drops of saturated ammonium carbonate solution to one part and 1-2 drops of sodium carbonate solution (~5%) to the other part. The yellow precipitate dissolves in both the reagents producing yellow solution due to the formation of tricarbonatouranilate (VI) ion :



The precipitated ammonium diuranate is also soluble in citric acid, tartaric acid and oxalic acid due to the formation of corresponding uranyl complexes.

(2) Sodium hydroxide solution

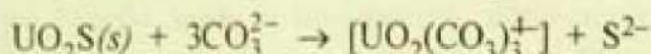
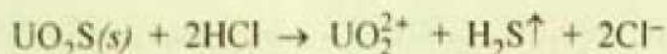
Take a drop of the test solution on a spot plate and add one drop of NaOH solution (~2M). Yellow precipitate of sodium diuranate ($Na_2U_2O_7$) is formed. Treat the precipitate with saturated ammonium carbonate solution. The precipitate dissolves, forming a yellow solution (*cf.* reaction with *aq-NH₃* discussed before).

(3) Ammonium sulfide solution

Place a drop of the test solution on a spot plate and add 1-2 drops of ammonium sulfide solution. Brown precipitate of uranyl sulfide (UO_2S) appears:



Divide the precipitate in two cavities of a spot plate using a dropper. Add dil.HCl to one cavity and saturated ammonium carbonate to the other cavity. The precipitate dissolves in both the reagents:



(5) Sodium (or ammonium) carbonate solution

Take a drop of the test solution in two adjacent cavities of a spot plate. Add one drop of dilute sodium carbonate solution (0.05 M) to one cavity and one drop of dilute ammonium carbonate solution to the other cavity. White precipitates of uranyl carbonate appear in both the cavities.



Now add 1-2 drops of concentrated solution (~0.5M) of Na_2CO_3 and a saturated solution of ammonium carbonate in either of the two cavities. The white precipitates in both the cavities dissolve, producing yellow solutions of tricarbonatouranylate (VI) ion (cf. reaction (1)).

(6) Disodium hydrogenphosphate solution

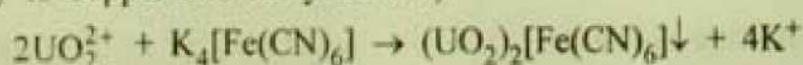
To a drop of the test solution in a semi-micro test tube add one drop of disodium hydrogen phosphate solution (~0.033 M). White precipitate of uranyl hydrogenphosphate, (UO_2HPO_4) appears. The precipitate is insoluble in dilute acetic acid but soluble in dilute mineral acids (HCl , HNO_3 , H_2SO_4).



If ammonium salts are present, ammonium uranyl phosphate ($(\text{NH}_4)\text{UO}_2\text{PO}_4$) is precipitated. On treatment with 0.5 M sodium phosphate (Na_3PO_4) solution, uranyl phosphate, $(\text{UO}_2)_3(\text{PO}_4)_2$ is precipitated, which exhibits a strong yellow fluorescence.

(7) Potassium ferrocyanide solution (~1%)

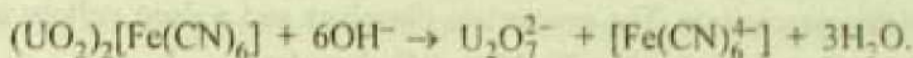
(a) To 1-2 drops of the neutral, or, acetic acid test solution on a spot plate, add 1-2 drops of potassium ferrocyanide solution. Brown precipitate of uranyl ferrocyanide, $(\text{UO}_2)_2[\text{Fe}(\text{CN})_6]$ appears (similarity to copper and molybdenum):



Divide the precipitate into two parts and place in two cavities of a spot plate and perform the following tests:

(i) To one part of the brown precipitate, add drops of dil.HCl. The precipitate dissolves (distinction from copper).

(ii) To the other part of the brown precipitate, add 1-2 drops of NaOH solution (~2M). The colour of the precipitate changes to yellow, as uranyl ferrocyanide is transformed to yellow coloured sodium diuranate ($\text{Na}_2\text{U}_2\text{O}_7$), setting free ferrocyanide ion (distinction from copper and molybdenum):



Alternatively, place a drop of the neutral or weakly acidic test solution on a drop reaction paper impregnated with 3% potassium ferrocyanide solution. A brown spot appears due to uranyl ferrocyanide.

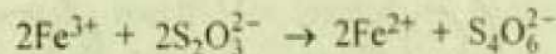
Limit of identification : 0.92γ of U

Limit of dilution : 1 : 5×10^4

Iron, copper and molybdenum interfere. Fe^{III} and Cu^{II} may be reduced to Fe^{II} and Cu^{I} by potassium iodide before addition of the ferrocyanide solution. The colour of the liberated iodine may be discharged by adding drops of sodium thiosulfate solution:



Reduction of Fe^{III} and Cu^{II} may also be carried out directly with sodium thiosulfate, when Cu^{II} acts as a catalyst for reduction of Fe^{III} (cf. p.-259, 370)



(b) Test of uranium in presence of iron and copper

Place a drop of concentrate (10%) KI solution on a drop reaction paper and allow the spot to dry. Add a drop of the neutral, or, weakly acidic test solution to the spot, followed by another drop of the KI solution for complete reduction. Allow the spot to dry and then add a drop of sodium thiosulfate solution (0.5 M) to discharge the iodine colour. Now add a drop of $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution to the decolourized spot. A brown ring due to uranyl ferrocyanide appears if uranium is present.

(c) Test of uranium in presence of Fe(III)

Take 1-2 drops of the test solution in a semi-micro test tube and add an excess of ammonium carbonate solution. If a precipitate (brown precipitate of $\text{Fe}(\text{OH})_3$, if $\text{Fe}(\text{III})$ is present) appears, centrifuge and discard the precipitate. If uranium is present, it remains in solution in the form of the carbonato complex, $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ion. Place one drop of the centrifugate on a drop reaction paper impregnated with 3% potassium ferrocyanide solution, a brown fleck results. Allow the paper to dry, and hold a dilute (1:1) HCl solution on the spot with the aid of a capillary tube. The brown colour becomes distinct at the edges of hydrochloric acid ring and a central Prussian blue stain may be visible if traces of iron is still present.

(8) Hydrogen peroxide

To a drop of the neutral or weakly acidic test solution on a spot plate, add 1-2 drops of 3% H_2O_2 solution. Pale yellow precipitate of hydrated uranium peroxide, $\text{UO}_2(\text{O}_2) \cdot 2\text{H}_2\text{O}$, or, uranium tetroxide, $\text{UO}_4 \cdot 2\text{H}_2\text{O}$, appears. Add drops of a saturated solution of ammonium carbonate to this precipitate. The precipitate dissolves and a deep yellow solution results. The test is sensitive for uranium, but Ti, V and Cr interfere.

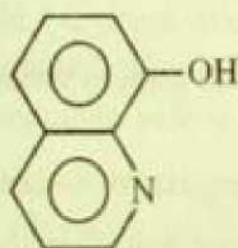
(9) Test with 8-hydroxyquinoline (Oxine)

Reagents:

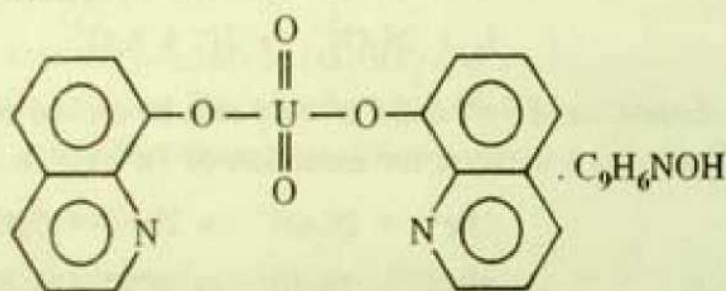
(i) 5% ethanolic solution of oxine.

(ii) Ammonium carbonate solution: Dissolve 2g. of ammonium carbonate in 10 ml of concentrated ammonia and then dilute with 10 ml of water.

Uranyl salts in neutral, or, in weakly alkaline solution react with 8-hydroxyquinoline (oxine, $\text{C}_9\text{H}_6\text{NOH}$, 1) to produce a red brown precipitate of composition, $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_6\text{NOH}$, containing two anionic and one neutral oxine species. In contrast to most metallic oxinates, which are inner complex phenolates, the uranium compound may be viewed as a dioxine ester of uranic acid, or, oxine uranate (2), rather than a uranyl oxinate.



(1)



(2)

Large number of metal ions which are precipitated as hydroxides in ammoniacal/alkaline medium and which form sparingly soluble oxinates interfere. But if the test is carried out after treating the test solution with an excess of ammonium carbonate solution, the test becomes almost specific for uranium. Because, in presence of a large excess of ammonium carbonate, uranium remains in solution as the carbonate complex, $[\text{UO}_2(\text{CO}_3)_3]^{4-}$ ion, whereas, all metal ions forming oxinates are precipitated either as carbonate or as hydroxide by alkaline carbonate. Thus, uranium can be separated from other metals before testing with oxine reagent.

Take 1-2 drops of the test solution in a semi-micro test tube and add an excess of ammonium carbonate reagent. Remove any precipitate at this stage by centrifuging. Place one drop of the clear centrifugate on a spot plate, or, on a drop reaction paper, and treat with a drop of 5% alcoholic solution of oxine. A red-brown precipitate or fleck appears if uranium is present.

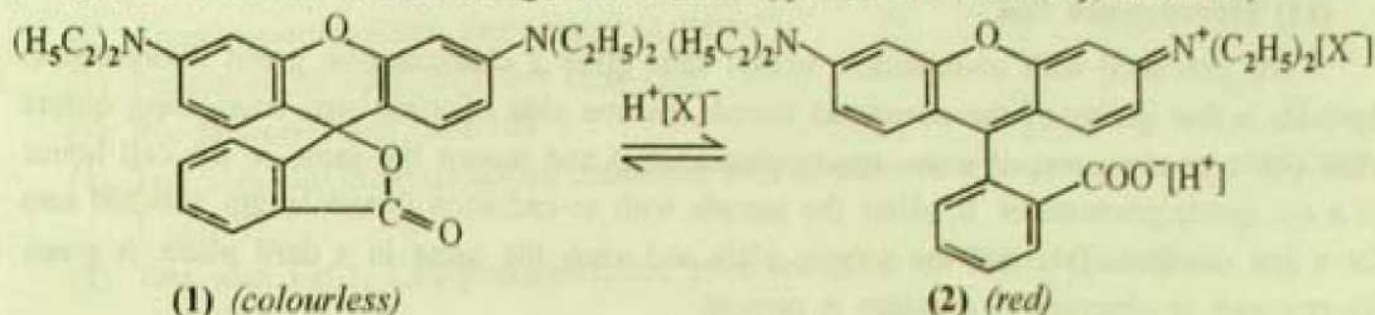
Limit of identification: 10γ of U

Limit of dilution : 1 : 5,000

(10) Test with Rhodamine B

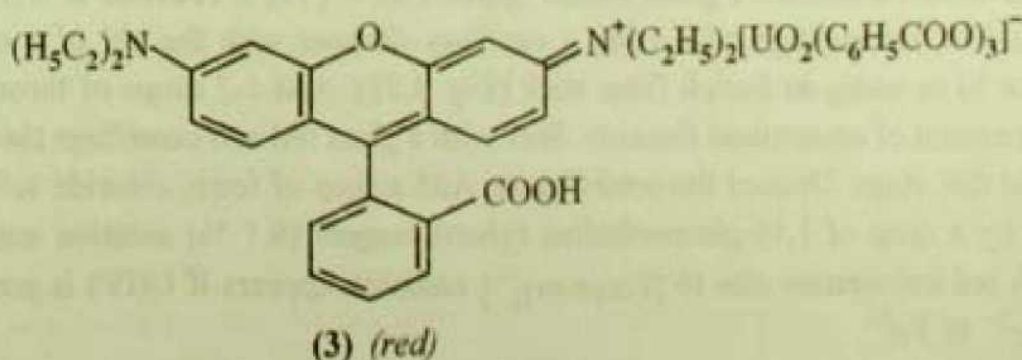
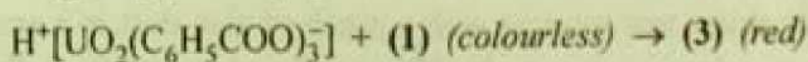
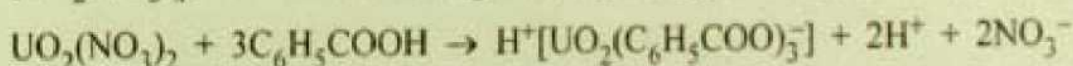
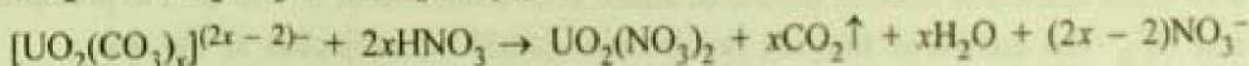
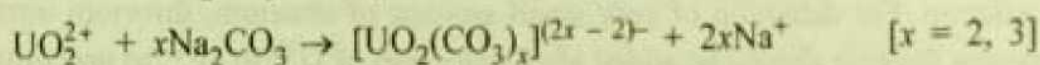
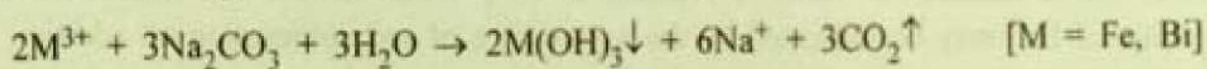
Reagent: Prepare a 0.5% solution of benzoic acid in benzene and treat this solution with an excess of rhodamine B reagent and then filter. Use the filtrate. The reagent keeps well.

Benzene solution of rhodamine B appears almost colourless, although, the colourless leuco form (1) and the red coloured quinoid form (2) of the reagent remain in equilibrium, which remains predominantly left shifted. In presence of acid solutions of monoprotic complex metal halogeno acids viz, $H[SbCl_6]$, $H[TlBr_4]$, $H[AuCl_4]$ etc. ($H[X]$ say) the equilibrium is shifted to the right and the benzene solution of the reagent becomes red coloured. When exposed to *uv* light, it shows an intense orange fluorescence (*cf.* tests for antimony, Sect. 4.9).



When colourless benzene solution of rhodamine B is shaken with neutral solutions of uranyl, ferric, or, bismuth nitrate (or chloride), the benzene layer turns red and also exhibits intense orange fluorescence when exposed to *uv* light. On addition of a little benzoic acid (C_6H_5COOH) or, any other benzene soluble organic acid, the red colouration of the benzene layer is highly intensified, possibly due to the formation of benzene soluble uranyl benzoic acid complex; which exists as a monoprotic complex acid, $H[UO_2(C_6H_5COO)_3]$, i.e., $H[X]$, and transforms the leuco form (1) of rhodamine B into the quinoid form (3).

The test can be made specific for uranium by treating the test solution with an excess of sodium carbonate solution, when Fe^{3+} and Bi^{3+} ions are precipitated as their hydroxides, but uranium remains in solution as its carbonate complex, $[UO_2(CO_3)_3]^{4-}$ or $[UO_2(CO_3)_2]^{2-}$ ions. Precipitate containing $Fe(OH)_3$ and $Bi(OH)_3$ should to be filtered or centrifuged off. The yellow coloured centrifugate is to be taken in a porcelain crucible and evaporated to dryness with nitric acid. The resulting residue contains uranyl nitrate, which is subjected to rhodamine B test.



Take a drop of the neutral test solution in a semi-micro test tube add 5 drops of the reagent solution and shake. The benzene layer turns red or pink depending upon the quantity of uranium present.

Limit of identifications: 0.05 γ of U

Limit of dilution : 1 : 1×10^6

(11) Fluorescence test

When irradiated with *uv*-radiation, uranyl salts gives a characteristic green fluorescence. Sprinkle a few grains of the powdered sample on one side of a moisten transparent quartz plate (or, a quartz cuvet of a *uv*- spectrophotometer) and mount the same in the cell house of a *uv*- spectrophotometer. Irradiate the sample with *uv*-radiation (wave length 360-200 nm) for a few minutes. Take out the sample plate and view the same in a dark place. A green fluorescence is observed if uranium is present.

Alternatively, take ~1 ml of the weakly acidic concentrated test solution in a quartz cell of a spectrophotometer and expose the same to *uv*-radiation for some time. View the cuvet in a dark place. A green fluorescence is observed if uranium is present. Intensity of the fluorescence is high in acidic solution but relatively low in basic solution.

(12) Test with fluorescein solution

Reagent: Shake 1 g of fluorescein with a mixture of 50 ml of ethanol and 50 ml of water, allow to stand for a day, filter and use the clear filtrate for the tests.

Place 1 drop of the test solution on a spot plate, add 1 drop of fluorescein reagent solution and 3 drops of 5% NH_4Cl solution. A red colouration results if uranium is present.

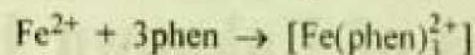
Limit of identification: 0.12 γ of UO_2^{2+} .

(13) Test after reduction of U^{VI} to U^{IV}

In weakly acidic solution U^{VI} maybe reduced to U^{IV} , which in turn can reduce Fe^{III} to Fe^{II} . Formation of Fe^{II} may be indicated by the appearance of red colouration on addition of 1,10-phenanthroline solution. For detection of very small amount of uranium, thorium nitrate along with some ammonium fluoride should be added after reduction of U^{VI} to U^{IV} , to precipitate ThF_4 and UF_4 . The combined fluoride precipitates should be subjected to the test.

Procedure

Stirr ~1 ml of the neutral or weakly acidic test solution with a pinch of zinc dust in a small beaker or a porcelain crucible. A green colour appears as U^{VI} is reduced to U^{IV} . Collect the clear liquid in a centrifuge tube using a capillary dropper with the aid of a cotton filter (Fig. 3.19 a or b) or using an Emich filter stick (Fig. 3.21). Add 1-2 drops of thorium nitrate (0.1 M) and a crystal of ammonium fluoride. Stirr with a glass rod and centrifuge the precipitate that appears at this stage. Discard the centrifugate. Add a drop of ferric chloride solution (~0.5 M) followed by a drop of 1,10-phenanthroline (phen) reagent (0.1 %) solution and stirr with a glass rod. A red colouration due to $[\text{Fe}(\text{phen})_3]^{2+}$ complex appears if U^{IV} is present, since it reduces Fe^{3+} to Fe^{2+} .



Limit of identification : 1γ of U.

Confirmation

- (1) Ammonia-ammonium carbonate test (test-1)
- (2) Pottassium ferrocyanide test (test-7)
- (3) Rhodamine-B test (test-10)
- (4) Test with 8-hydroxyquinoline combined with ammonia-ammonium carbonate test (tests 1 and 9)
- (5) Test with FeCl_3 -1,10-phenanthroline after reduction to U(IV), (test-13)

Observation	Probable substance
White precipitate formed on addition of NH_4OH to the solution.	UO_2^{2+}
White precipitate formed on addition of $\text{K}_4\text{Fe}(\text{CN})_6$ to the solution.	U^{4+}
Reddish-brown color developed on addition of FeCl_3 to the solution.	U^{4+}
Reddish-brown color developed on addition of FeCl_3 to the solution after reduction with Zn .	U^{4+}
Reddish-brown color developed on addition of FeCl_3 to the solution after reduction with Zn and addition of NH_4OH .	U^{4+}
Reddish-brown color developed on addition of FeCl_3 to the solution after reduction with Zn and addition of NH_4OH and H_2O .	U^{4+}
Reddish-brown color developed on addition of FeCl_3 to the solution after reduction with Zn and addition of NH_4OH and H_2O and HCl .	U^{4+}

CHAPTER - 9

Qualitative Analysis of Unknown Inorganic Mixtures by Spot Reactions

9.1 Introduction

Spot tests are very useful in preliminary examinations. It is always advisable to carry out preliminary tests to obtain some general information regarding the nature of the sample before proceeding to systematic analysis. The observations of the spot reactions are important in establishing the presence, or, absence of certain substances, in making intelligent choice of solvents, reaction conditions etc. Spot reactions are often successfully applied directly on solid samples, or, to evaporation residues, insoluble residues and also to liquid samples and solutions.

9.2 Examination of Physical Characters of the Sample

Physical characters, such as colour, odour, texture (i.e crystalline or, amorphous), hygroscopic, or, deliquescent nature, colour of aqueous, acidic, or, alkaline extracts; acidity or alkalinity of the aqueous extract etc. often give preliminary indications about the radicals present in the sample. Compare the colour of the sample or, its constituents with the list of colored compounds (*cf.* Sect.,6.2). Examine the aqueous extract of the sample with litmus paper (better with pH paper or, Universal indicator paper) and note the acidity, or, alkalinity of the extract. Record all these observations and formulate preliminary inferences.

Physical Characters	Observations	Probables/Inferences
(a) Solid Sample		
(i) Colour	Characteristic colour (to be stated)	Transition metals also Pb, As, Sb, Bi, Sn, Cd etc.
(ii) Odour	Smells NH_3 Smells H_2S	NH_4^+ salts S^{2-}
(iii) Texture	Crystalline Amorphous	Metal salts, NH_4^+ salts Metal oxides, silicates, borates phosphates, carbonates etc.
(b) Aqueous extract		
(i) Acidity or alkalinity	Acidic	Hydrolysed metal salts, NH_4^+ salts, acid salts: H_2PO_4^- , HF_2^- , HSO_4^- .
	Alkaline	Soluble CO_3^{2-} , HPO_4^{2-} , PO_4^{3-} , metal oxides, hydroxides.

Physical Characters	Observations	Probables/Inferences
b(i) (Contd.)	Neutral	Alkali, alkaline earth metal salts with strong acids.
(ii) Colour	Coloured	Mostly transition metal ions.
	Blue/green	Cu^{2+} , Ni^{2+} , Cr^{3+} , Fe^{2+} , $(\text{V}^{\text{IV}})^*$
	Purple/pink	Co^{2+} , MnO_4^- ,
	Yellow/orange	CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ Fe^{3+} , $(\text{UO}_2^{2+}, \text{Ce}^{4+})^*$
	Yellow/brown	$(\text{BrO}_3^- + \text{Br}^-)$, $(\text{IO}_3^- + \text{I}^-)$ etc. with acidic ingredient.
	Red	$(\text{Fe}^{3+} + \text{SCN}^-)$, $(\text{Mo}^{3+} + \text{SCN}^-)^*$

9.3 Preliminary Tests Directly on the Solid Sample

Perform the tests with a minute quantity of the sample and record only the actual observations.

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
1.	Ignition test (Cf. Sect. 6.3 for details)	(a) Sublimation (b) Colour change (c) Melting (d) Evolution of coloured gas with characteristic odours: (i) brown vapour (ii) violet vapour (iii) smells NH_3 (iv) smells H_2S (v) smell of burning S	NH_4^+ , Hg, As. Transition metal Pb, Zn, Sn Na^+ , K^+ , Mg^{2+} salts Br^- , NO_3^- , NO_2^- I^- NH_4^+ + basic substance S^{2-} + acidic substance SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$

*Rare elements

Sl No.	Experiments/ Reagents	Observations		Probables/ Inferences
2.	Flame test (cf. Sect. 6.5)	Naked eye	Double blue glass	Na K Ca Sr Ba, Mo* Cu, Borate
		Golden yellow Violet Brick red Crimson Yellowish-green Green	Colourless Red/Crimson Light green Purple Bluish-green	
3.	Borax bead test (cf. Sect 6.6)	Bead colour in oxidizing flame (O.F.), reducing flame (R.F.) in hot (h) and cold (c) conditions. (record the actual observations only).		
		O.F.	R.F.	
	(a) Common elements	(i) Green (h), blue (c)	Colourless (h), opaque red (c)	Cu
		(ii) Yellow-brown (h) yellow (c)	Bottle green (h & c)	Fe
		(iii) Yellow (h), green (c)	Green (h & c)	Cr
		(iv) Blue (h & c)	Blue (h & c)	Co
		(v) Violet (h), amethyst (c)	Colourless (h & c)	Mn
		(vi) Violet (h), redish brown (c)	Grey (h & c)	Ni
	(b) Rare elements	(vii) Yellow (h) colourless (c)	Yellow (h) yellow-brown (c)	W
		(viii) Yellow (h) pale yellow (c)	Green (h) Bottle green (c)	U
		(ix) Yellow (h) greenish yellow (c)	Brownish (h) Emerald-green (c)	V
		(x) Yellow (h) colourless (c)	Grey (h) Pale violet (c)	Ti
		(xi) Orange-red (h) colourless (c)	Colourless (h & c)	Ce

*Rare elements

Sl No.	Experiments/ Reagents	Observations		Probables/ Inferences
4.	Microcosmic salt bead test (cf. Sect 6.7)	Colour of the bead in oxidizing flame (O.F.), reducing flame (R.F.) under hot (h) and cold (c) conditions (record the actual observations only).		
		O.F.	R.F.	
	(a) Common elements	(i) Green (h) blue (c)	Colourless (h) red (c)	Cu
		(ii) Yellow-redish brown (h) yellow (c)	Yellow (h) Colourless to green (c)	Fe
		(iii) Green (h & c)	Green (h & c)	Cr.
		(iv) Blue (h & c)	Blue (h & c)	Co
		(v) Violet (h & c)	Colourless (h&c)	Mn
		(vi) Brown (h & c)	Grey (c)	Ni
	(b) Rare elements	(vii) Yellow (h & c)	Green (c)	V
		(viii) Yellow (h) yellow-green (c)	green (h & c)	U
		(ix) Pale yellow (h) colourless (c)	Green (h) Blue (c)	W
		(x) Colourless (h&c)	Yellow (h) violet (c)	Ti
5.	(a) Oxidative fusion test: Sample + Fusion mixture + KNO_3 heated to fusion (cf. Sect. 6.8)	The colour of the fused mass after solidification : (i) Yellow (ii) Green		Cr Mn
	(b) Aqueous extract of fused mass (a) treated with:			
	(i) Acetic acid + Pb-acetate	Yellow precipitate (PbCrO_4)		Cr
	(ii) HNO_3 + NaBiO_3	Pink colouration (MnO_4^-)		Mn

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
6.	Stable sodium stannite solution added to the solid sample or, its <i>aq</i> -suspension, or <i>aq</i> -solution.	Immediate blackening occurs	Ag, Hg, Bi
7.	<i>Aq</i> -NH ₃ solution added to solid sample or its <i>aq</i> -suspension/ <i>aq</i> -solution (other than black coloured sample)	Immediate blackening	Hg(I)
8.	(H ₂ O ₂ + NaOH)	(i) Bleaching (ii) Blackening/darkening	S ²⁻ Mn, Co, Ni, Fe, Cu
9.	(H ₂ O ₂ + HCl)	Bleaching	PbO ₂ , MnO ₂ , S ²⁻
10.	(NH ₃ + "AgOH")	Blackening	Mn, Co, Ni, Fe, Cu
11.	H ₂ S-water + HCl (<i>cf.</i> Group separation, Sect. 7.8)	Coloured precipitate	H ₂ S-Group metals (Groups-I, IIA, IIB)
12.	(NH ₄) ₂ S	Coloured precipitate	Group-IIA & Group-IIIB metals, Fe, Cr.
13.	Dilute H ₂ SO ₄	Evolution of gases: (i) Colourless odourless gas, turning lime-water milky. (ii) Colourless gas with smell of burning sulfur, turns lime-water milky, discharges the blue colour of starch I ₂ paper. (iii) Colourless gas with smell of rotten eggs, turns lead acetate paper black. (iv) Brown vapour, turns starch-iodide paper blue.	CO ₂ from CO ₃ ²⁻ SO ₂ from SO ₃ ²⁻ and or S ₂ O ₃ ²⁻ H ₂ S from S ²⁻ NO ₂ from NO ₂ ⁻

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
14.	Conc.H ₂ SO ₄ + heat	Evolution of gases: (i) Oily bubbles sticking to the wall of test tube, turning water drop opaque. (ii) White vapour, turns blue litmus paper red, forms dense white fumes with NH ₃ (iii) Brown vapour, turns starch-iodide paper blue. (iv) Violet vapour	HF, SiF ₄ from F ⁻ , HF ₂ ⁻ HCl from Cl ⁻ Br ₂ from Br ⁻ , NO ₂ from NO ₃ ⁻ , NO ₂ ⁻ . I ₂ from I ⁻
15.	Conc.H ₂ SO ₄ + Cu - T + heat	Brown vapour	NO ₂ from NO ₃ ⁻ , NO ₂ ⁻
16.	Conc-H ₂ SO ₄ + MnO ₂ + heat	(i) Greenish yellow gas, turning starch-iodide paper blue. (ii) Brown vapour, turning starch iodide paper blue. (iii) Violet vapour	Cl ₂ from Cl ⁻ Br ₂ from Br ⁻ I ₂ from I ⁻
17.	Conc.H ₂ SO ₄ + K ₂ Cr ₂ O ₇ + heat (chromyl chloride test for chloride) (cf. Sect. 6.12)	Yellow brown vapour, turns NaOH solution yellow, which on acidification with acetic acid forms yellow precipitate with lead acetate solution.	CrO ₂ Cl ₂ from Cl ⁻
18.	Conc.H ₂ SO ₄ + KCl + heat (chromyl chloride test for chromate, dichromate)	Same observation as test-17	CrO ₂ Cl ₂ from CrO ₄ ²⁻ , Cr ₂ O ₇ ²⁻
19.	Conc.H ₂ SO ₄ + CaF ₂ (in Pb-crucible) + heat (cf. Sect. 6.18)	Dense white vapour, turns water drop on Pt-loop opaque	SiF ₄ from SiO ₃ ²⁻ , SiO ₂
20.	Conc. H ₂ SO ₄ + EtOH/warm and ignite the issuing vapor. (cf. Sect. 6.14)	Vapour burns with green edged flame	B(OCH ₃) ₃ from BO ₃ ³⁻ , H ₃ BO ₃
21.	EtOH/heat and ignite the issuing vapour	Same as test -20	B(OCH ₃) ₃ from H ₃ BO ₃

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
22.	(NaOH + Zn/Al)/ heat	Smell of NH_3 , turning (i) moist phenolphthalin paper red, the red colour is discharged on drying the paper. (ii) Nessler's reagent paper brown. (iii) MnSO_4 - Ag_2SO_4 paper black. (iv) $\text{Hg}_2(\text{NO}_3)_2$ paper black.	NH_3 from NH_4^+ , NO_2^- , NO_3^-
23.	NaOH/heat	Same as test-22	NH_3 from NH_4^+
24.	I_2 -KI- NaN_3 solution (Catalysis of iodine-azide reaction).	(i) Discharge of I_2 colour with evolution of colourless odourless gas (N_2) (ii) Discharge of I_2 colour without gas evolution. (iii) Evolution of gas without discharge of I_2 colour.	S^{2-} , $\text{S}_2\text{O}_3^{2-}$, SCN^- Reducing agents Oxidizing agents

In the above tests, record only the actual observations and formulate inference accordingly. Search for the radicals carefully which are indicated from these preliminary tests. Clearly record the experiments, observations and inferences for the positive tests only. For the negative tests, record the clause "*no characteristic observation*" in the observation column and the word, "*inconclusive*" in the inference column.

9.4. Tests with Aqueous Suspension of the Sample

These test may be carried out on the spot plate, filter paper strips, or, in semi-micro test tubes, or, in semi-micro centrifuge tubes as required for a particular test. Record only the actual observations and inferences.

Note: These tests may give preliminary indications about the radicals present.

Sl. No.	Experiments/Reagents	Observations	Probables/Inferences
1.	Colour of <i>aq</i> -extract (Perform individual tests based on the colour of <i>aq</i> -extract)	(i) Yellow-orange (ii) Pink/purple (iii) Green (iv) Blue	CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, Fe^{3+} (Ce^{4+} , UO_2^{2+})* $\text{Co}^{2+}(\text{aq})$, MnO_4^- $\text{Cr}^{3+}(\text{aq})$, $\text{Ni}^{2+}(\text{aq})$, $\text{Fe}^{2+}(\text{aq})$ $[\text{VO}^{2+}(\text{aq})]$, $\text{Cu}^{2+}(\text{aq})$, $[\text{VO}^+(\text{aq})]^*$

*Rare elements

Sl. No.	Experiments/Reagents	Observations	Probables/Inferences
2.	Indicator paper/pH-paper/litmus paper	(i) Acidic (ii) Alkaline	H_3BO_3 , HF_2^- , NH_4^+ , HSO_4^- , $H_2PO_4^-$, hydrolyzed salts of Hg^{2+} , Fe^{3+} , Al^{3+} , Cr^{3+} (Ti^{4+} , Zr^{4+} , Ce^{4+})* Anions of weak acids: CO_3^{2-} , SO_3^{2-} , HPO_4^{2-} , free bases: PO_4^{3-} , OH^- , O^{2-} .
3.	$Ni^{II}(DMGH)_2$ -equilibrium solution	Red precipitate of $Ni(DMGH)_2$	Basic/alkaline AsO_4^{3-} , CrO_4^{2-} , CO_3^{2-} , PO_4^{3-} , (soluble/insoluble)
4.	Dilute HCl	(i) Formation of white precipitate (ii) Appearance of brown colour (iii) Appearance of dark brown colour or, dark violet precipitate. (iv) Formation of yellow/orange precipitate from alkaline <i>aq</i> -extract. The precipitate dissolves in alkali carbonate or yellow $(NH_4)_2S_x$ solution. (<i>cf.</i> Sect. 7.8)	Hg_2^{2+} , Ag^+ , Pb^{2+} Br^- + oxidant (Br^- + BrO_3^-) I^- + IO_3^- (or other oxidants) Sulfides of As, Sb, Sn (Group-IIB)
5.	(KI + starch)/dil. H_2SO_4	Blue colouration	Oxidants for ($2I^- \rightarrow I_2$)
6.	(Fe^{II} -salt + NH_4SCN)/dil.HCl (Note: If Fe^{III} is absent)	Red colouration [$Fe^{III}(SCN)^{2+}$]	Oxidants for $Fe^{II} \rightarrow Fe^{III}$
7.	(I_2 -KI-starch) + dil.acetic acid (blue solution)	Discharge of blue colour	Reductants for $I_2 \rightarrow 2I^-$
8.	(NaN_3 + I_2 + KI + starch) blue solution (iodine-azide test)	(i) Decolourization with gas evolution (ii) Only decolourization (iii) Only gas evolution	SCN^- , $S_2O_3^{2-}$, S^{2-} Reductants Oxidants

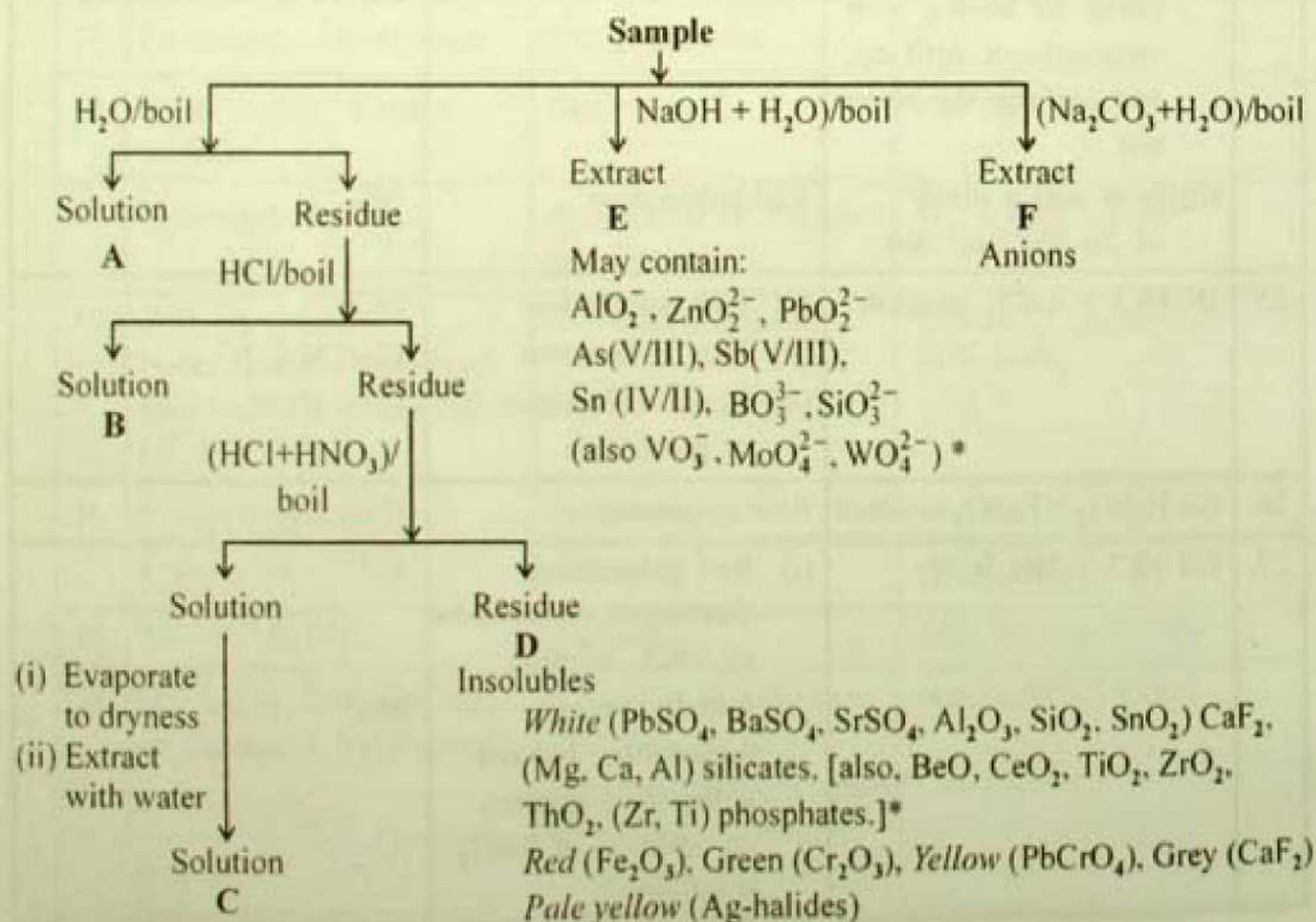
Sl. No.	Experiments/Reagents	Observations	Probables/Inferences
9.	(Ag ^I -ferrocyanide + Fe ^{III} -sulfate)/dil.H ₂ SO ₄	Blue colouration or precipitate	Cl ⁻ , Br ⁻ , I ⁻
10.	HNO ₃ + AgNO ₃	Appearance of (i) white to yellow precipitate (ii) Black precipitate (iii) Yellow precipitate, turning brown to black. (iv) Orange red precipitate soluble in NH ₃ .	Cl ⁻ , Br ⁻ , I ⁻ , SCN ⁻ , IO ₃ ⁻ , BrO ₃ ⁻ . S ²⁻ S ₂ O ₃ ²⁻ [Fe(CN) ₆] ³⁻
11.	NaOH + Na-nitroprusside solution	Violet colouration	S ²⁻
12.	Zn-nitroprusside solution	Red colouration	SO ₃ ²⁻
13.	Stable sodium stannite solution	Blackening	Ag, Hg, Bi
14.	H ₂ S-water/dil.HCl	Appearance of coloured precipitate	H ₂ S group metals
15.	(NH ₄) ₂ S solution Note: Perform individual tests with the precipitate (cf. Sect 7.8)	Coloured precipitate	Metals of Group-I, IIA, IIIB, Fe ^{III} , Cr ^{III} .
16.	H ₂ O ₂ + NaOH	Darkening	Mn, Fe, Co, Ni, Cu
17.	H ₂ O ₂ + HCl	Bleaching	PbO ₂ , MnO ₂ , S ²⁻
18.	NH ₃ + "AgOH"	Darkening	Mn, Fe, Co, Ni, Cu
19.	(Al-foil or Davardas alloy or Zn-dust + NaOH)/boil	Evolution of NH ₃ gas. Test with (i) HCl, (ii) Phenolphthalin paper, (iii) Nessler's reagent paper (cf. Sect. 9.3/22)	NH ₄ ⁺ , NO ₃ ⁻ , NO ₂ ⁻
20.	NaOH/boil	Same as test - 19	NH ₄ ⁺

Sl. No.	Experiments/Reagents	Observations	Probables/Inferences
21.	Conc.HCl/boil	Deep green colouration Deep blue colouration	Co, Cr V*
22.	Aq-NH ₃ solution	(i) Deep blue colouration (ii) Blackening (iii) Precipitation (iv) Complete dissolution	Cu, Ni, Hg ₂ ²⁺ Inconclusive Insoluble Ag salts [#]
23.	Conl. HNO ₃ + NaBiO ₃ /heat	Purple colouration (MnO ₄ ⁻)	Mn
24.	Tests for NO ₃ ⁻ and NO ₂ in mixture: (cf. Sects. 5.3, 5.4) (i) Sulfanilic acid + α -nathylamine. (ii) If a red colouration appears, decompose nitrite by boiling with urea/sulfamic acid etc. and perform the above test. (iii) Now add a pinch of Zn-dust and stirr.	Red colouration No red colouration Red colouration	NO ₂ ⁻ NO ₂ ⁻ absent (i.e. removed) NO ₃ ⁻
25.	Dil.HCl + FeCl ₃ solution	(i) Red colouration (ii) Blue colouration (iii) Brown colouration or precipitate	SCN ⁻ [Fe(CN) ₆ ⁴⁻] I ⁻
26.	Dil.H ₂ SO ₄ + FeSO ₄ solution	Blue colouration	[Fe(CN) ₆ ³⁻]
27.	Dil HCl + NH ₄ SCN	(i) Red colouration, discharged on addition of SnCl ₂ solution. (ii) Initially no red colouration, but red colouration appears on addition of SnCl ₂ solution.	Fe ³⁺ Mo*

Except AgBr, AgI. *Rare elements

Sl. No.	Experiments/Reagents	Observations	Probables/Inferences
28.	Saturated K_2SO_4 solution/ boiled	White precipitate	Pb^{2+} , Ba^{2+} , Sr^{2+} (also Th^{4+} , Zr^{4+})*
29.	Phosphoric acid + oxalic acid + sulfuric acid (POS) reagent + NH_3 until alkaline.	(i) White precipitate (ii) No precipitate	Gr I to IV & Mg^{2+} May be Na^+ , K^+
30.	Titan yellow test for Mg^{2+} if the test 29 is negative (cf. Sect. 4.21)	Red colouration or precipitate	Mg^{2+}
31.	$NaClO_4$ or, $HClO_4$ solution	White crystalline precipitate	K^+ , NH_4^+
32.	Sodium cobaltinitrite test.	Crystalline yellow precipitate	K^+ , NH_4^+

9.5 Scheme for Preparation of Solutions for Wet Tests

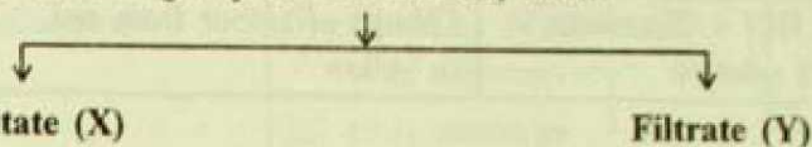


*Rare elements

9.6 Detection of Anions Radicals in the Na_2CO_3 -Extract (F)

Prepare the *neutralized Na_2CO_3 -extract* as described earlier (*cf.* Sect 7.3) and proceed as follows.

Take ~5 ml of the neutralized Na_2CO_3 extract in a small beaker add drops of a concentrated solution of $\text{Zn}(\text{NO}_3)_2$. If a precipitate appears, add more $\text{Zn}(\text{NO}_3)_2$ solution until precipitation is complete. Warm the mixture gently for 2-3 minutes, filter.



- Precipitate (X)**
1. Wash with a little hot-water while still on the filter paper
 2. Directly test for anion radicals using the washed precipitate following scheme-1 (below)

- Filtrate (Y)**
1. Test for anion radicals following scheme-2 (below)

Scheme-1:

Tests for anion radicals in the precipitate-X

Perform the following tests directly with the precipitate (X) on a spot plate or on a filter paper strip or in a semi-micro test tube as required (*cf.* Sect. 7.3): Record the experiments, actual observations and inferences accordingly.

Sl No.	Experiments/ Reagents	Observations Precipitation/colouration/spot	Probables/ Inferences
1.	(a) Acetic acid + lead acetate (b) Acetic acid + CdSO_4 solution (c) Na-nitroprusside + NaOH	Black Yellow Violet	S^{2-} S^{2-} S^{2-}
2.	Dil. H_2SO_4 + FeSO_4 (or Mohr's salt) solution	Blue	$[\text{Fe}(\text{CN})_6]^{3-}$
3.	Dil. HCl + FeCl_3	Blue	$[\text{Fe}(\text{CN})_6]^{4-}$
4.	Ammonium molybdate + HNO_3 + benzidine + NH_4 - acetate	Blue	PO_4^{3-}
5.	Gutzeit test (<i>cf.</i> Sect. 4.8)	Blackening of AgNO_3 paper by the issuing gas	AsO_4^{3-} , AsO_3^{3-}
6.	(a) Quinalizarin test in presence of conc. H_2SO_4 . (<i>cf.</i> Sect. 5.20)	Violet to blue	BO_3^{3-} , H_3BO_3 B_2O_3

Sl No.	Experiments/ Reagents	Observations Colouration/spot	Probables/ Inferences
6.	(b) (Curcuma-HCl) (cf. Sect. 5.20)	Bluish green colour appears, colour disappears on adding NaOH solution.	BO_3^{3-}
7.	$\text{BaCl}_2 + \text{HCl} + \text{Zirconium -}$ Alizaris-S solution	Change of colour from red to yellow	F^-

Scheme -2:

Tests for anion radicals in filtrate-Y

Perform the following tests with the filtrate (Y) on a spot plate, or on a filter paper strip or in a semi-micro test tube as required.

Sl No.	Experiments/ Reagents	Observations Colouration/precipitation/spot	Probables/ Inferences
1.	(a) Colour	Yellow	CrO_4^{2-}
	(b) Acetic acid + Lead acetate	Yellow precipitate	CrO_4^{2-}
2.	(a) Dil. H_2SO_4 + Diphenylcarbazide	Violet colouration	CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$ [MoO_4^{2-}]*
	(b) Dil. H_2SO_4 + H_2O_2 (6%) + ether	Blue etherial layer	CrO_4^{2-} , $\text{Cr}_2\text{O}_7^{2-}$
3.	(a) Dil. HNO_3 + dil. KMnO_4 + $\text{Ba}(\text{NO}_3)_2$ solution, centrifuge. Add a few crystals of oxalic acid	Pink coloured precipitate. Pink colour of supernatant solution is discharged, but the precipitate remains pink coloured.	SO_4^{2-} SO_4^{2-}
	(b) Red coloured Ba-rhodizonate suspension on a spot paper + solution-Y.	Decolourization of red flecks	SO_4^{2-}
4.	Fuchsin-bisulfite solution (spot plate) + Cl_2 -water	Blue-violet colouration	Br^-
5.	$\text{HCl} + \text{FeCl}_3$ solution	Intense red colouration	SCN^-
6.	I_2 -KI-starch blue solution (on spot plate)	Dicharge of blue colour (i) Decolourised solution tests acidic to blue litmus.	S^{2-} , SO_3^{2-} , $\text{S}_2\text{O}_3^{2-}$ SO_3^{2-}

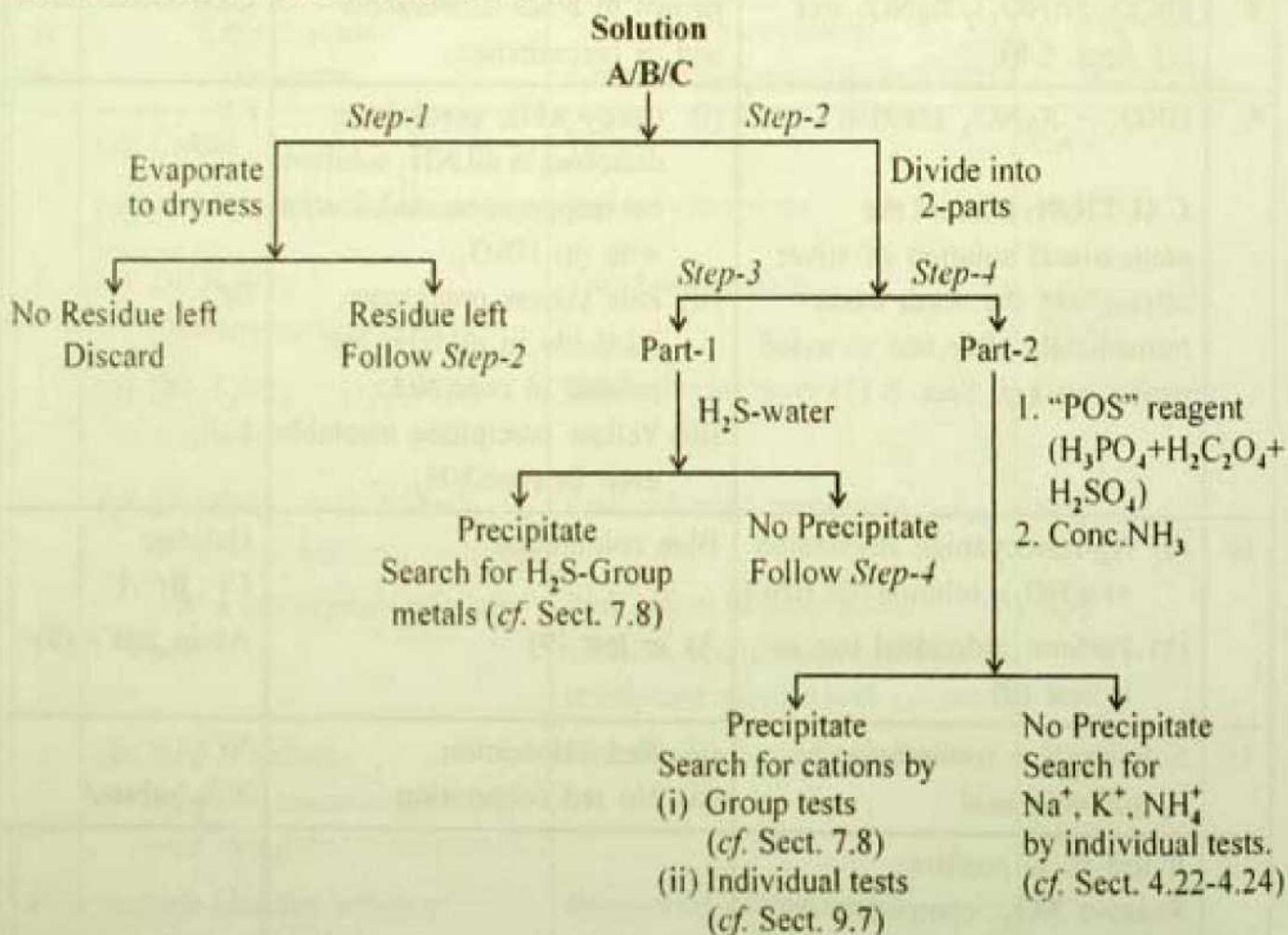
*Rare elements

Sl No.	Experiments/ Reagents	Observations Colouration/precipitation/spot	Probables/ Inferences
6.		(ii) Decolourised solution tests neutral to litmus (blue remains blue, red remains red).	$S_2O_3^{2-}$, S^{2-}
7.	Catalysis of iodine-azide reaction.	(i) Discharge of blue colour with effervescence (ii) Only discharge of blue colour, without effervescence (iii) Only effervescence without discharge of blue colour	S^{2-} , $S_2O_3^{2-}$, SCN^- Reductant Oxidant
8.	$PbCO_3/Sr(NO_3)_2/AgNO_3$ test (cf. Sect. 5.8)	Brown to black colouration and or precipitation.	$S_2O_3^{2-}$
9.	$HNO_3 + AgNO_3$ solution CAUTION: Discard the ammoniacal solution of silver nitrate into the wash basin immediately after test to avoid explosion. (cf. Sect. 5.11)	(i) Curdy white precipitate, dissolves in dil. NH_3 solution, but reappears on acidification with dil HNO_3 . (ii) Pale yellow precipitate, insoluble in dil. NH_3 but soluble in conc. NH_3 . (iii) Yellow precipitate insoluble even in conc. NH_3 .	Cl^- Br^- I^-
10.	(a) Ag-ferrocyanide suspension + $Fe(NO_3)_3$ solution + dil. HNO_3 (b) Perform individual test as in test (9)	Blue colouration As in test (9)	Halides: Cl^- , Br^- , I^- As in test - (9)
11.	Solution-Y + α -naphthylamine + sulfanilic acid.	(i) Red colouration (ii) No red colouration	NO_2^- NO_2^- -absent
12.	If test-11 is positive: Remove NO_2^- completely by boiling the solution -Y with urea/sulfamic acid/ NH_4Cl , (a) Perform test-11 with the resulting solution. (b) Add a pinch of Zn-dust and repeat test-11.	(i) No red colouration (ii) Red colouration	NO_2^- absent (i.e, removed) NO_3^- present

9.7 Wet Test Scheme for Detection of Cation Radicals

(a) With solutions A/B/C

Before proceeding to carry out wet tests for cations, it is desirable to see whether the test solution at all contains any dissolved material. This may be easily ensured by evaporating a drop of the test solution to dryness by gentle warming in a clean test tube or in a porcelain basin. If no residue is left, the test solution does not contain any dissolved salt. If a residue is left, the test solution contains some dissolved salts(s). Now, whether the dissolved salts are of the cations other than the alkali metal ions (Na^+ , K^+) and NH_4^+ , that may be ensured by treating the test solution with (i) H_2S -water, (ii) mixture of phosphoric acid, oxalic acid and sulfuric acid (POS-reagent) rendered ammoniacal. If any precipitate is formed with these two reagents, some cation(s) other than Na^+ , K^+ and NH_4^+ ions must be present. If no precipitate is formed with these reagents, the solution should be tested for Na^+ , K^+ and NH_4^+ ions only. The procedure is schematically shown below.



Wet tests for cations in solutions A/B/C

Systematic Group-analysis for wet tests for cations have already been discussed before (cf. Sect.-7.8). These will not be repeated here. Individual semi-micro tests for cations are summarized below in experiment-observation - inference format. These tests may be carried out in semi-micro test tubes, on spot plates and on spot reaction papers (Whatman No. 1 filter paper strips) as required for a particular test, as described in for individual cation radicals (Ch - 4).

Sl No.	Experiments/ Reagents	Observations Colouration/precipitation/spot	Inferences/ Probables
1.	Colour of solution	Coloured (i) Blue-green (ii) Yellow-orange	Transition metals Cu, Cr, Co, Ni, Fe Fe ^{III} , Cr ^{VI} , (U ^{VI} , Ce ^{IV})*
2.	Conc. HCl/heat	(i) Intense blue-green (ii) Intense red-brown	Co, Cr Fe(III)
3.	Conc. NH ₃	(i) Intense blue (ii) Brown precipitate (iii) Blackening	Cu, Ni Fe(III) Hg(I)
4.	NH ₄ SCN test	(i) Red (ii) Blue	Fe(III) Co
5.	K ₄ [Fe(CN) ₆] test (i) HCl medium (ii) Acetic acid medium	Intense blue Chacolate/brown	Fe(III) Cu, [Mo, U]*
6.	K ₃ [Fe(CN) ₆]/HCl	Blue	Fe(II)
7.	1,10-phenanthroline (If test 6 is positive)	Red	Fe(II).
8.	Diphenylcarbazide test (cf. Sect. 4.13, 5.18 and 8.8)	Violet colouration	Cr, [Mo]*
9.	DMGH ₂ -tartaric acid-NH ₃	Red precipitate	Ni
10.	α -Nitroso- β -naphthol test (cf. Sect 4.14)	Red precipitate	Co
11.	NaBiO ₃ + HNO ₃ /warm	Pink colouration appears, discharged by oxalic acid	Mn
12.	(a) H ₂ S-water/HCl, or, ZnS-paper (b) (NH ₄) ₂ S-solution	Black Brownis-black Yellow-orange Coloured precipitate Bi, Co, Ni, Mn	Cu, Hg, Pb, Ag Bi Cd, As, Sb, Sn Cu, Ag, Pb, Hg,
13.	Sodium stannite solution	Blackening	Ag, Hg, Bi
14.	Gutzeit's test: Solution + Zn + HCl/heat (cf. Sect 4.8)	Blackening of AgNO ₃ paper by the issuing gas	As

*Rare elements

Sl No.	Experiments/ Reagents	Observations Colouration/precipitation/spot	Inferences/ Probables
15.	Rhodamine-B test in conc. HCl, after oxidation with NaNO_2 (cf. Sect. 4.9)	Blue -violet colouration	Sb.
16.	(Ammonium phosphomolybdate-benzidine-ammonium acetate) test - after reduction with (Zn-HCl), or, (Al-HCl) (cf. Sect. 4.10)	Blue	Sn
17.	$[\text{Fe}(\text{bipyridine})_3]_2$ - test in ammoniacal solution (cf. Sect 4.7)	Red spot/ring	Cd
18.	Conc. $(\text{NH}_4)_2\text{CO}_3\text{-NH}_3$	White precipitate	Ba, Sr, Ca, Pb, Cd
19.	Saturated K_2SO_4 or $(\text{NH}_4)_2\text{SO}_4$ solution	White precipitate Note: Apply flame test with the precipitate. (cf. Sect. 4.4, 4.8, 4.19)	Ba, Sr, Pb
20.	K_2CrO_4 -acetic acid (after neutralization with <i>aq</i> - NH_3)	Yellow precipitate	Ba, Pb
21.	Sodium rhodizonate test	(i) Blue-violet spot, changes to scarlet with tartaric acid-tartrate buffer ($\text{pH} \sim 2.8$) (ii) Red-brown stain	Pb. Ba, Sr
22.	Sodium rhodizonate +NaOH	Violet spot	Ca
23.	Alizarin-S test (cf. Sect. 4.12)	Red lake	Al
24.	(a) $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4] + \text{CuSO}_4$ (b) $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4] + \text{Co}(\text{NO}_3)_2$ (c) $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4] + \text{ZnSO}_4$	Violet Blue (i) Violet (ii) Blue	Zn Zn Cu Co
25.	Titan yellow + NaOH (cf. Sect. 4.21)	Red	Mg
26.	Quinalizarin + NaOH (cf. Sects. 4.21, 8.2)	Blue	Mg, [Be*]

*Rare elements

Sl No.	Experiments/ Reagents	Observations Colouration/precipitation/spot	Inferences/ Probables
27.	Zincuranylacetate test (cf. Sect. 4.22)	Shining crystalline yellow precipitate	Na
28.	Sodium cobaltinitrite test (cf. Sect. 4.23)	Yellow precipitate	K, NH_4^+
29.	Sodium cobaltinitrite- AgNO_3 test. (cf. Sect. 4.23)	Yellow precipitate	K, NH_4^+
30.	NaClO_4 or dil. HClO_4 solution	White crystalline precipitate	K, NH_4^+
31.	Sodium tetraphenyl boron test	White precipitate	K, NH_4^+
32.	NaOH/boil	NH_3 evolved, which turns (i) red litmus paper blue (ii) colourless phenolphthalin paper red (iii) Nessler's reagent paper brown (iv) AgNO_3 - MnSO_4 paper black	NH_4^+
33.	If tests (28-32) are positive, remove NH_4^+ ion from the test solution by boiling with NaOH solution until the observations in test 32 are all negative. Now, perform tests (28-31) with the resulting solution after neutralization with dilute acetic acid/HNO_3 as required. (a) Test - 28 (b) Test - 29 (c) Test - 30 (d) Test - 31	Yellow precipitate Yellow precipitate White crystalline precipitate White precipitate	K K K K

Notes:

1. If H_2S group metals are present (Test 12(a) and or (b) are positive), go for separation of Groups I, IIA, IIB and IIIB (cf. Sect. 7.8)
2. If test 18 is positive and test 12(a) is negative, go for separation as Group-IV. (cf. Sect. 7.8). Also search for uranium (rare element).

3. If test for Al and Zn (tests 23, 24(a), 24(b)) are positive, perform these tests also with the NaOH-extract (E) for confirmation.
4. Tests for Mg (tests 25, 26) are to be carried out after removal of NH_4^+ ion and most cation radicals other than Na^+ , K^+ . The following procedure is recommended for isolation of Mg.

Take 2-3 ml of the test solution A/B/C in a test tube, add drops of H_2S -water. If a precipitate is formed dilute and add more H_2S -water until precipitation is complete. Gently warm the mixture and filter/centrifuge, discard the precipitate. Boil the filtrate/centrifugate to expel H_2S completely. If no precipitate is formed on addition of H_2S water, discard the solution and proceed with a fresh portion.

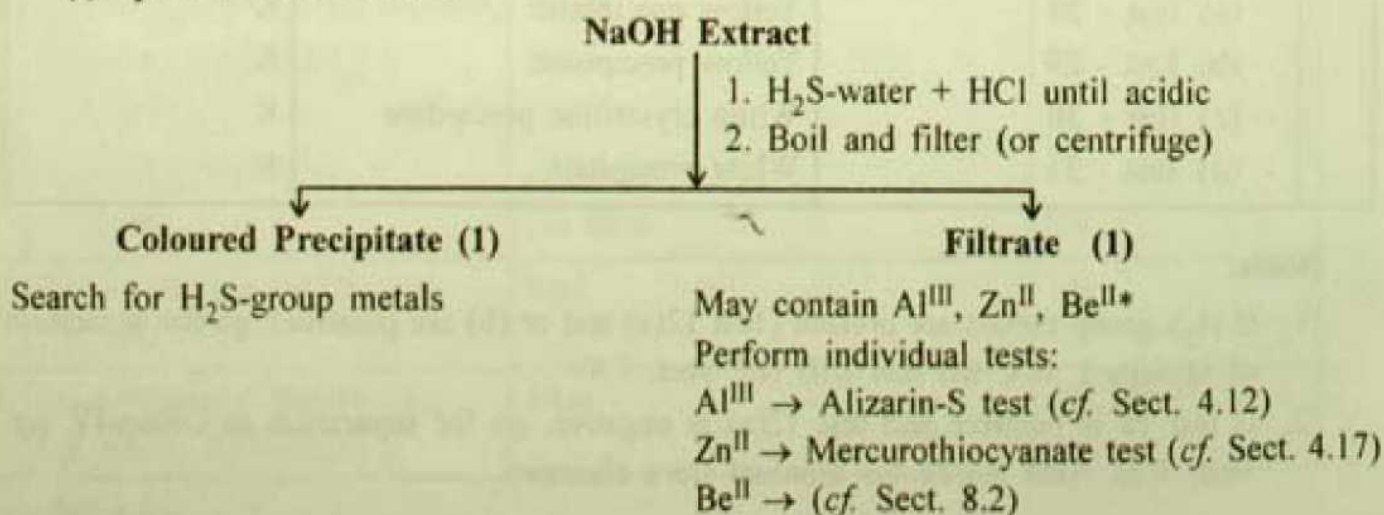
Add a few drops of Br_2 -water, or, Cl_2 -water and boil gently for a few minutes to oxidize Fe(II), if any, to Fe(III). Omit this step if iron is absent. Add ~1 ml of a mixture of phosphoric acid-oxalic acid-sulfuric acid mixture (POS-reagent). Neutralize the solution with dilute NH_3 avoiding excess and make the solution just acidic by adding very dil. HCl (pH ~4.5, test with a pH - paper strip).

Now add 2-3 ml of acetic acid-ammonium acetate buffer solution (pH ~4.5) and warm the mixture gently for 1-2 minutes. Filter/centrifuge off any precipitate and add drops of neutral FeCl_3 solution to precipitate the unreacted phosphate completely as FePO_4 . Finally add drops of aq- NH_3 until ammoniacal to precipitate the unreacted Fe^{3+} ions completely as $\text{Fe}(\text{OH})_3$. Warm gently for 1-2 minutes and filter/centrifuge off the precipitate. Evaporate the resulting solution to dryness in a porcelain basin. Moisten the residue with a few drops of conc. HNO_3 and heat the mixture strongly in side a **FUME CUPBOARD** to decompose and expel ammonium salts completely. Cool and add a few drops of water and warm gently to dissolve the salt, $\text{Mg}(\text{NO}_3)_2$. Test for Mg^{2+} with this prepared solution (cf. Sect. 4.21).

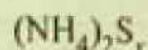
(b) West tests for metallic ions with the NaOH extract (E)

The NaOH extract may contain metallic elements which form amphoteric and acidic oxides. Systematic as well as individual tests are to be performed for detection of metallic ions in the NaOH extract.

(i) Systematic Procedure



Coloured Precipitate (1)



Residue

PbS (black)

Hot
dil.HNO₃

Solution

Search for Pb by individual tests.
(cf. Sect. 4.4)

Solution

May contain thio-salt formers:

As, Sb, Sn (V, Mo, W)*

HCl

Coloured Precipitate

As₂S₅, Sb₂S₅, SnS₄ (cf. Sect. 7.8).
(V₂S₅, MoS₃, WS₃)* - perform
individual tests. (cf. Sect. 8.7-8.9)

(ii) Individual tests on the NaOH-extract (E)

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
1.	H ₂ S-water/HCl	(i) Black precipitate (ii) Yellow-orange-brown precipitate	Pb As, Sb, Sn (V, Mo, W)*
2.	If a black precipitate is formed in test (1), perform the following tests with the solution-E (cf. Sect. 4.4). (i) Acetic acid+K ₂ CrO ₄ (ii) Acetic acid+KI (iii) Dil.H ₂ SO ₄ +Alcohol	Yellow precipitate (PbCrO ₄) Yellow crystalline precipitate (PbI ₂) Heavy white precipitate (PbSO ₄)	Pb Pb Pb
3.	If a yellow-orange precipitate is formed in test (1) perform the following tests with the solution-E or with the precipitate.		

*Rare elements

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
3.	(i) (Zn+HCl)/AgNO ₃ Gutzeit's test (<i>cf.</i> Sect. 4.8) (ii) Rhodamine-B test (<i>cf.</i> Sect. 4.9) (iii) Ammonium phosphomolybdate test (<i>cf.</i> Sect. 4.10)	Blackening Blue-violet colouration Blue colouration	As Sb Sn
4.	Alizarin-S test ¹ (<i>cf.</i> Sect. 4.12)	Red lake formation	Al
5.	Mercuriothiocyanate test: (Acetic acid + (NH ₄) ₂ [Hg(SCN) ₄] + CuSO ₄ solution	Violet precipitate	Zn

Note: (1) Phosphate interferes in alizarin-S test for Al by precipitating AlPO₄ under the condition of the test. If phosphate is present, add drops of BaCl₂ solution to the NaOH extract to precipitate phosphate completely as barium phosphate. Filter/centrifuge, discard the precipitate and perform alizarin-S test with the resulting solution.

9.8 Identification of Insoluble Residues (D)

Sl No.	Experiments/ Reagents	Observations Colouration/precipitation/spot	Probables/ Inferences
1.	Colour Note: Compare with the of colours of common inorganic materials (<i>cf.</i> Sect.-6.2)	Blue Green Red Chacolate Yellow Ash Pale yellow White	Fe ₄ [Fe(CN) ₆] ₃ Cr ₂ O ₃ Fe ₂ O ₃ Cu ₂ [Fe(CN) ₆] PbCrO ₄ CaF ₂ SnO ₂ , Ag-halides Zn ₂ [Fe(CN) ₆] Inconclusive
2.	Green Insoluble (a) Try bisulfate fusion, extract with water. Oxidize with: (i) 30% H ₂ O ₂ /NaOH (ii) K ₂ S ₂ O ₈ -AgNO ₃ -H ₂ SO ₄ (b) Diphenycarbazide test with oxidised solution (a) (ii)	(i) Yellow colour (ii) Orange colour (b) Violet colour	Cr ₂ O ₃ Cr ₂ O ₃ Cr ₂ O ₃

Sl No.	Experiments/ Reagents	Observations/Colouration/ Precipitation/Spot etc.	Probables/ Inferences
2.	(c) Acetic acid+Pb-acetate test with oxidised solution(a)(i)	(c) Yellow precipitate	Cr_2O_3
3.	Red Insoluble Prepare bisulfate fusion extract as in test-2. Test for Fe(III) directly with on the extract. (i) $\text{K}_4[\text{F}(\text{CN})_6]$ (ii) NH_4SCN	Blue Red	Fe_2O_3 Fe_2O_3
4.	Yellow Insoluble (PbCrO_4) Extract with conc. NaOH solution. (a) Acidify the extract with acetic acid, add $\text{Ba}(\text{NO}_3)_2$ solution (b) Acidify with HNO_3 add conc. $(\text{NH}_4)_2\text{SO}_4$ solution	Yellow solution Yellow precipitate White precipitate, dissolves on boiling with conc. solution of ammonium acetate.	CrO_4^{2-} CrO_4^{2-} Pb^{2+}
5.	Pale yellow insoluble (a) NH_4I /heat (Fume Cupboard) (b) <i>Luminescence reaction:</i> $\text{D} + \text{Zn}/\text{HCl}$, stirr with a test tube full of cold water, hold the test tube in non-lumimons flame. (c) Sulfur fusion. Fusion extract + HCl (cf. Sect. 4.10)	Completely volatilizes Blue luminescence Yellow precipitate	SnO_2 SnO_2 SnO_2
6.	(a) $\text{K}_4[\text{Fe}(\text{CN})_6] + 2,2'$ -bipyridine + NH_3 (b) If test 6(a) is positive, proceed as follows: Reduce with Zn-dust+dil. H_2SO_4 . Filter and test for halides in the filtrate with AgNO_3 solution. Test the solubility of the precipitate in NH_3 solutions.	Red colouration Curdy white-yellow precipitate (i) soluble in dil. NH_3 (ii) soluble in conc. NH_3 (iii) insoluble even in conc. NH_3	Ag-halides Cl^- Br^- I^-

Sl No.	Experiments/ Reagents	Observations/Colouration/ Precipitation/Spot etc.	Probables/ Inferences
6.	(c) Dissolve the residue of test 6(b) in dil. HNO_3 , add dil. HCl . (d) Extract the insoluble residue-D with sodium thio sulfate solution and search for Ag^+ and halides in the extract by individual tests.	Curdy white precipitate soluble in dil. NH_3 (cf. Sects. 4.2, 5.8, 5.11-5.13)	Ag^+ (cf. Sects. 4.2, 5.8, 5.11-5.13)
7.	White Insoluble Flame test after reduction in the reducing flame. (cf. Sect. 6.5)	Apple green flame Crimson red flame	BaSO_4 SrSO_4 , CaF_2
8.	Alizarin-S test on NaOH -extract (cf. Sect. 4.17)	Red lake	Al_2O_3
9.	Conc. ammonium acetate solution (boil). (i) Solution + K_2CrO_4 (ii) Solution + KI (iii) Solution + $\text{Ba}(\text{NO}_3)_2$ solution	Dissolves completely Yellow precipitate Yellow crystalline precipitate dissolves on boiling, reappears on cooling White precipitate	PbSO_4 Pb^{2+} Pb^{2+} SO_4^{2-}
10.	Fusion with fusion mixture, extraction of the fused mass with water. (a) <i>Tests with the fusion extract:</i> Acidify with dil. HNO_3 and perform the following tests: (i) Add $\text{Ba}(\text{NO}_3)_2$ solution. (ii) Alizarin-S test (iii) $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]$ + CuSO_4 solution (iv) H_2S -water	 White precipitate Red lake Violet precipitate Yellow precipitate	 SO_4^{2-} Al^{3+} Zn^{2+} Sn

Sl No.	Experiments/ Reagents	Observations/Colouration/ Precipitation/Spot etc.	Probables/ Inferences
	(b)(i) D + CaF_2 + conc. H_2SO_4 in a lead crucible, warm gently, absorb the issuing gas in a drop of water held on a Pt-wire loop. (ii) Apply benzidine blue-molybdenum blue test with the opaque water drop following the same procedure as in 11(a). Compare with a blank.	Water drop turns opaque. Blue colouration.	SiO_2, SiO_3^{2-} SiO_2, SiO_3^{2-}
12.	Test for CaF_2 (a)(i) Mix D with conc. H_2SO_4 in a dry test tube and heat gently. Absorb the issuing gas in a drop of water held at the head of a glass rod. (ii) Apply benzidine blue-molybdenum blue test with the opaque water drop following the same procedure as in 11(a). Compare with a blank. (b)(i) Digest the insoluble residue with conc. H_2SO_4 as in 12(a) in a Fume Cupboard until white fumes (SiF_4, HF) ceases to appear. Cool and pour the resulting cold reaction mixture into ~10 ml of water contained in a beaker. Cool and filter. Add conc. NH_3 until ammoniacal and then a saturated solution of $(\text{NH}_4)_2\text{CO}_3$.	Oily bubbles appear and the water drop turns opaque. Blue colouration White precipitate	F^- F^- Ca

Sl No.	Experiments/ Reagents	Observations/Colouration/ Precipitation/Spot etc.	Probables/ Inferences
	(ii) Apply flame test with the precipitate of the above test, 12(b)(i).	Transient brick red flame	Ca
13.	Tests for insoluble ferrocyanides: $\text{Cu}_2[\text{Fe}(\text{CN})_6]$, $\text{Zn}_2[\text{Fe}(\text{CN})_6]$, $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$. Extract with hot conc. NaOH solution. $[\text{Fe}(\text{CN})_6]^{4-}$ and zinc as ZnO_2^{2-} ion occur in the alkaline extract. Iron and copper occur in the residue as hydrous oxides/hydroxides. (a) Tests on the NaOH extract: (i) HCl/FeCl_3 (ii) Acetic acid+ $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]$ + very dilute CuSO_4 (b) Dissolve the residue in dil. 5M HNO_3 solution. Test for Cu(II) and Fe(III) directly with this solution. Treat the solution with the following reagents: (i) $\text{HCl}/\text{NH}_4\text{SCN}$ (ii) $\text{HCl}/\text{K}_4[\text{Fe}(\text{CN})_6]$ (iii) $\text{HCl}/\text{H}_2\text{S}$-water (iv) Conc. NH_3 solution. (v) Deep blue solution obtained in (iv) + Acetic acid + $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution.	Blue colour or precipitate Violet precipitate Red coloration Blue colouration or precipitate Black precipitate Deep blue colouration Chalolate precipitate insoluble in acetic acid but decomposes in solutions of alkali.	$[\text{Fe}(\text{CN})_6]^{4-}$ Zn Fe Fe May be Cu Cu Cu

9.9 Tests for Rare Elements*

(a) Tests with aqueous or acid extracts (A/B/C)

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
1.	HCl + NH_4SCN + SnCl_2	(i) Red colouration (ii) Blue	Mo W
2.	Dilute H_2SO_4 + H_2O_2	(i) Wine red colouration, not discharged by fluoride ion. (ii) Yellow colouration, discharged by fluoride, reappears on boiling with H_3BO_3 .	V Ti
3.	(i) KHSO_4 – H_2SO_4 - phenol (Defacq test) (cf. Sect. 8.9) (ii) SnCl_2/HCl (iii) Zn/HCl (tungsten blue test) (cf. Sect. 8.9)	Redish violet colouration Blue colouration Blue colouration	W W W
4.	(i) $\text{K}_4[\text{Fe}(\text{CN})_6]$ + acetic acid (ii) $(\text{NH}_4)_2\text{CO}_3$ – NH_3 test (cf. Sect. 8.10)	Brown precipitate, dissolves in dil HCl, turns yellow on addition of NaOH solution. Yellow precipitate, dissolves in excess of the reagent.	U U
5.	If both Mo and W are suspected. Perform HCl – NH_4SCN – SnCl_2 test on a filter paper strip. (cf. Sects. 8.8, 8.9)	Blue central spot (for W) and red ring on the periphery for (Mo).	W and Mo
6.	(a) NaK-tartrate + H_2O_2 (b) AgNO_3 – NH_3 (c) Anthranilic acid	Brown precipitate, turns yellow on boiling. Black precipitate Blakish blue precipitate, rapidly passes into solution which turns brown.	Ce Ce (III) Ce (IV)

* For P.G. Level Experiments

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
7.	Quinalizarin test in faintly alkaline medium (<i>cf.</i> Sect. 8.2)	Corn flower blue colour, not discharged by Br_2 -water	Be
8.	(a) Alizarin-S test in acidic medium (<i>cf.</i> Sect. 8.4)	Red colouration, discharged by fluoride ion	Zr
	(b) <i>p</i> -Dimethylaminobenzene azophenylarsonic acid/dil. HCl (<i>cf.</i> Sect. 8.4)	Brown precipitate/spot	Zr
9.	H_3PO_4 -dil. H_2SO_4	White precipitate	Ti, Zr.
10.	Oxalic acid/ NH_4 -oxalate	White precipitate i) insoluble in excess reagent ii) soluble in excess reagent iii) soluble in dil.HCl/ H_2SO_4 iv) insoluble in dil.0.5M HCl v) dissolves in large excess of NH_4 -oxalate, but reappears on addition of dil.0.5M HCl.	Zr, Ce, Th Ce, Th Zr Zr Th, Ce Th

(b) In NaOH Extract (E)

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
1.	H_2S water + dil.HCl	Brown precipitate, dissolves in yellow $(\text{NH}_4)_2\text{S}_x$	V, Mo, W
2.	Dil. H_2SO_4 - H_2O_2	Wine red colouration, not discharged by fluoride	V
3.	HCl- NH_4SCN - SnCl_2 If both Mo and W are suspected try capillary separation test on filter paper (<i>cf.</i> Sects. 8.8, 8.9)	(i) Red colouration (ii) Blue colouration Central blue spot (W) with red ring on the periphery (Mo)	Mo W W & Mo
4.	(a) HCl - SnCl_2 (b) Zn - HCl (c) KHSO_4 - H_2SO_4 phenol/heat (<i>Defacqz reaction</i>) (<i>cf.</i> Sect. 8.9)	Blue Blue Red	W W W

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
5.	(a) Dilute with a large volume of water and boil.	White precipitate appears, dissolves on addition of HCl	Be
	(b) Quinalizarin test (cf. Sect 8.2)	Cornflower blue colouration not discharged by Br ₂ - water.	Be

(c) In Na₂CO₃ Extract (F)

Perform the following tests with the precipitate (X) obtained on treatment of the neutralized Na₂CO₃ extract with Zinc nitrate solution.

Sl No.	Experiments/ Reagents	Observations	Probables/ Inferences
1.	SnCl ₂ solution	Yellow to brown colouration	MoO ₄ ²⁻ , WO ₄ ²⁻
2.	HCl-NH ₄ SCN-SnCl ₂ (on spot paper)	Central blue spot Peripheral red ring	WO ₄ ²⁻ , MoO ₄ ²⁻
3.	HCl - Potassium ethylxanthate	Violet colouration or precipitate	MoO ₄ ²⁻
4.	Dil.H ₂ SO ₄ + H ₂ O ₂ (on spot plate or in test tube)	Wine red colouration not discharged on addition NH ₄ HF ₂ .	VO ₃ ⁻

9.10 Formulation of Probable Compositions of Inorganic Mixtures

After the detection and confirmation of the cation and anion radicals, the next and the final step in qualitative inorganic analysis is to formulate the probable composition of the sample, based on tests and reasonings. For this purpose, some additional tests may required to be carried out. The following stepwise procedure may be followed.

1. First of all, list the detected cation and the anion radicals as they occur in the different parts of the sample, e.g.,

- | | | |
|--------------------------|-------------|------------|
| (i) Water soluble part: | Cation | Anion |
| (ii) Acid soluble part : | Cation | Anion |
| (iii) Insoluble part : | Cation ... | Anion |

2. Then formulate tentative compositions with the cations and anions detected in a particular part of the sample, according to the valency of the respective ions.

Anions which are not detected in the aqueous part, but are detected in the Na₂CO₃ - extract, may be combined with the cations detected in the acid soluble part (also those in the insoluble part in some cases).

If no anion is detected in a particular part, the cation(s) that is (are) detected in that part, probably exist(s) as oxides, hydroxides, carbonates, or bicarbonates etc., which are not recognized as detectable anion radicals. Occurance of carbonate, or, bicarbonate is indicated from the evolution colourless odourless effervescence (CO_2) on treatment of the sample with dilute acid ($\text{dil.HCl/H}_2\text{SO}_4/\text{HNO}_3$).

3. If the sample dissolves in water, partly or completely, note the colour of the aqueous solution and test its acidity or alkalinity with litmus papers (blue and red) or with pH paper.

Acidic aqueous solutions result from the deprotonation of various (i) protonated anions, viz, HF_2^- , H_2PO_4^- , HSO_4^- etc. and (ii) aquated high positively charged metal ions, i.e, metallo-acids, viz, $[\text{Fe}(\text{H}_2\text{O})_6^{3+}]$, $[\text{Al}(\text{H}_2\text{O})_6^{3+}]$, $[\text{Cr}(\text{H}_2\text{O})_6^{3+}]$, $[\text{Ti}(\text{H}_2\text{O})_6^{4+}]$, $[\text{Ce}(\text{H}_2\text{O})_6^{4+}]$, $[\text{Zr}(\text{H}_2\text{O})_6^{4+}]$, $[\text{Be}(\text{H}_2\text{O})_4^{2+}]$ * etc.

NH_4^+ ion, if present with strong acid anions such as NO_3^- , SO_4^{2-} , Cl^- etc. renders the aqueous solution weakly acidic (cf. Sect. 2.1)

Presence of water soluble salts of strongly basic anions viz, CO_3^{2-} , F^- , PO_4^{3-} , AsO_4^{3-} , AsO_3^{3-} , BO_3^{3-} , NO_2^- , SO_3^{2-} render the aqueous extract of the sample alkaline. Some protonated anions, e.g, HCO_3^- , HPO_4^{2-} etc. give weakly basic reactions in aqueous solution.

Therefore, from examination of acid-base nature of the aqueous extract, it may be possible to decide the exact form in which these anions, if present, exist in the sample.

4. Certain elements may exist in more than one oxidation states, but are detected in the form of a particular oxidation state. The exact oxidation state and the particular form in which the element occurs in the sample may be determined by additional tests and reasonings. In any case, all the forms of a particular element will be considered as a single radical.

Examples (9.1): Common elements

(i) Mercury (Hg)

Mercury may exist as Hg^{I} and Hg^{II} , both are detected by the same tests, eg, with SnCl_2 or with sodium stannite. But Hg^{I} undergoes disproportionation to Hg^{II} and Hg^0 in presence of ammonia and dilute alkali.

(ii) Arsenic (As)

Arsenic may occur as As^{III} or As^{IV} sulfides and oxides and also as arsenite (AsO_3^{3-}) and arsenate (AsO_4^{3-}) respectively. All forms of arsenic respond to Gutzeit test and also to ammonium molybdate test under the conditions of these tests. But only arsenite, AsO_3^{3-} , form white precipitate with ammoniacal solution of magnesium chloride or magnesia mixture.

(iii) Iron (Fe)

Iron may exist as Fe^{II} and Fe^{III} . There are specific reagents for testing these radicals. Fe^{II} salt solutions are bottle green, whereas, Fe^{III} , salt solutions may have a range of colours, ranging from colourless through yellow to violet.

*Rare elements

(iv) Chromium (Cr)

Chromium may occur as Cr^{III} and Cr^{VI} . Cr^{III} compounds are green to violet in colour. Cr^{VI} compounds are yellow-orange in colour, eg. CrO_4^{2-} (yellow), $\text{Cr}_2\text{O}_7^{2-}$ (orange). From the action of $\text{Ni}(\text{DMgH})_2$ - equilibrium solution, one may decide whether Cr^{VI} is present as chromate or as dichromate. (cf. Sect. 5.18)

(v) Manganese (Mn)

Manganese may occur as Mn^{II} -salts, MnO_2 , Mn^{VI} (manganate) and Mn^{VII} (permanganate). Mn^{II} -salts and their solutions are almost colourless or light pink coloured, whereas, manganates (MnO_4^{2-}) are green and permanganates (MnO_4^-) are purple. Mn^{IV} is best known in the form of black MnO_2 . Mn^{II} salts are devoid of any redox property. MnO_2 and permanganates (eg. KMnO_4) are strongly oxidizing and manganates (Na_2MnO_4) readily disproportionate to permanganate and MnO_2 .

Examples (9.2) : Rare elements*

Among the rare elements Be, Ti, V, Mo, W, Zr, Ce, U and Th, only V, Mo, W, U and Ce in their air stable compounds may exist in more than one oxidation states. Be^{II} , Ti^{IV} , Zr^{IV} , Th^{IV} are the only stable oxidation states of these elements and all compounds derived from these ions are white in colour. Oxides of all these four metals are insoluble, white coloured powders, whereas, their salts such as sulfates, nitrates/oxy nitrates, chlorides/oxy chlorides are soluble in water.

(i) **Cerium (Ce):** May occur as Ce^{III} and Ce^{IV} . Ce^{III} compounds are white and non oxidizing, whereas, Ce^{IV} compounds are yellow in solid state and in solution and are strongly oxidizing.

(ii) **Uranium (U):** May occur as U^{IV} and U^{VI} in the forms of oxides : UO_2 (brownish-black), UO_3 (orange-yellow), U_3O_8 (greenish black), etc. and also as uranyl (UO_2^{2+}) salts $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$. Uranyl salts are bright yellowish coloured in solid state and in solutions.

(iii) **Vanadium (V):** Metavanadates (V^{V} , VO_3^-) and the oxide, V_2O_5 , are most common vanadium (V) compounds. V_2O_5 is almost colourless, but when dissolved in acid, it produces light yellow solution. Vanadyl (VO^{2+}) compounds are green. Vanadium (2+) state is violet and very strongly reducing.

(iv) **Molybdenum (Mo):** Mo^{III} , Mo^{V} and Mo^{VI} states are common and stable. Mo^{VI} state occur in most of the common molybdenum compounds. Molybdic acid, $\text{MoO}_3 \cdot \text{H}_2\text{O}$ ($\equiv \text{H}_2\text{MoO}_4$) gives weakly acidic aqueous solution. Molybdates of alkali metals and NH_4^+ are soluble in water. Lead molybdate is sparingly soluble. In combination with phosphate, silicate etc., molybdate forms heteropoly acids, eg, phosphomolybdic acid, $\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$, which gives acidic reaction in aqueous solution although it is associated with phosphate. Mo^{V} compounds are blue coloured and in most cases these are mixed valent compounds. So, even if phosphate and molybdate are present from different sources in the same sample, they will be transformed in to phosphomolybdic acid in acidic solution and will occur as simple phosphate and molybdate in alkaline solution.

(v) **Tungsten (W):** It mainly exists in W^{VI} state as tungstic acid, $\text{WO}_3 \cdot x\text{H}_2\text{O}$ and tungstate salts eg, $\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$. Tungstates, like molybdates also form heteropoly acids in combination with phosphoric acid, boric acid and silicic acid and often exists as salts of such heteropoly

acids. Heteropolytungstates are formed in acidic solution. Phosphotungstic acid $H_3[PO_4(W_{12}O_{36})]$ or $H_3[P(W_3O_{10})_4]$ gives acidic reaction in aqueous solution. In alkaline medium the heteropolyanions break in to simple anions. W^V compounds are blue coloured and in most cases these are mixed valent compounds.

So, to ascertain the exact form in which these elements occur in the sample, some additional test may required to be carried out.

5. When more than one cation radicals are detected in a particular part of the sample, more than one tentative compositions maybe formulated, form which the most probable composition may be assigned by considering the physical nature of the sample and acid-base and redox properties and colour of its solutions.

Example (9.3)

Suppose Cd^{2+} , Zn^{2+} , S^{2-} and PO_4^{3-} ions are detected in the acid soluble part of the sample. The tentative compositions that may arise out of these radicals are:

- (i) CdS , $Zn_3(PO_4)_2$
- (ii) CdS , ZnO , $Cd_3(PO_4)_2$
- (iii) $Cd_3(PO_4)_2$, ZnS
- (iv) CdO , ZnS , $Zn_3(PO_4)_2$

Sine the colour of CdS is yellow, CdO is brown coloured and the remaining compounds, ZnO , ZnS , $Cd_3(PO_4)_2$ and $Zn_3(PO_4)_2$ are all white coloured, the colour of the mixtures (i) and (ii) will be light yellow to yellow depending upon the proportion of CdS . Colour of the mixture (iii) will be white, whereas, colour of the mixture (iv) will be light brown to brown depending upon the proportion of CdO . Therefore, consideration of colour also may give clues to the most probable composition.

6. Some times it is not even posible to arrive at a single composition for a mixture even after considering the physical nature and also the chemical behaviour of the sample.

Example (9.4)

Suppose Mg^{2+} , K^+ , Cl^- and SO_4^{2-} are detected in the aqueous extract and found in the same solution. The tentative compositions may be :

- (i) $MgCl_2$, K_2SO_4
- (ii) $MgCl_2$, $KHSO_4$
- (iii) $Mg(HSO_4)_2$, KCl
- (iv) $MgSO_4$, KCl

Since $MgCl_2$ is hygroscopic, whereas, KCl , $MgSO_4$, $KHSO_4$, $Mg(HSO_4)_2$ are not, the physical nature of the sample may again be taken into consideration. If the sample appears moisten, it may be due to hygroscopic nature of $MgCl_2$, suggesting the compositions (i) or (ii). If the sample appears dry and granular, it may be either (iii) or (iv). Since bisulfate ion (HSO_4^-) is strongly acidic, whereas, SO_4^{2-} and Cl^- ions are neutral, so are the hydrated K^+ and Mg^{2+} ions, acid-base property of the aqueous solution gives further clues to the most probable composition. If the aqueous extract is neutral, its composition should be (iv). If the

sample appears moisten and its aqueous solution is acidic, its composition should be (ii) and if its aqueous solution is neutral, its composition should be (i).

If water of crystallization is indicated in the ignition test with the dry and granular sample (iv), its composition may be $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, KCl , since magnesium sulfate exists as $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. If the aqueous extract of the sample is alkaline, then carbonate/bicarbonate of either of the two metals (Mg, K) may be also present as additional radicals.

Some more examples will be discussed in the next section.

9.11 Reporting Sheet for Qualitative Analysis of Unknown Model Inorganic Mixtures

The purpose of this section is to provide a guide-line to the beginners in qualitative analysis of complex inorganic mixtures, for recording experimental procedures, observations, formulating conclusions, or, inferences in a short but systematic manner. The findings during a laboratory session may be initially recorded in a "rough copy" of the *Laboratory Note Book* in an abbreviated manner on day to day basis, immediately after performing each individual experiment or test. At the end of each laboratory session, the students should report their findings to their class teachers/laboratory instructors and discuss with them any problem, or, any new observation they have come across during the days work, so that these problems may be addressed during the next laboratory session.

After the analysis of a sample is complete, the experiments, observations, inferences and conclusions on the probable composition of the sample may be clearly recorded accordingly in the "fair copy" of the *Laboratory Note Book*. Both fair copy and the rough copy of the laboratory note books should be submitted to the teacher for observation/correction/evaluation purpose as the case may be.

The following abbreviations may be used in recording the experimental procedures, observations and inferences on the rough copy of the laboratory note book.

Abbreviations	Descriptions
NCO	No characteristic observation
INC	Inconclusive
(+)	Test positive, expected change(s) observed
(-)	Test negative, expected change(s) not observed
↓	Precipitation occurs
↑	Gas evolution occurs
Δ	Heating/warming
Radical (✓)	Radical present
Radical (×)	Radical absent
Radical (Cf)	Radical confirmed
Radical (~)	Radical may be present (suspected)

Since these abbreviations are not Universally used/recommended, their descriptions are to be clearly stated, whenever, these are applied in the recording.

After the analysis is complete, the cation and the anion radicals and the insoluble materials if any detected, should be clearly stated along with the charges of the radicals. Preliminary tests, wet tests and/or confirmatory tests of the detected radicals should be clearly described in the laboratory note book. Special tests indicating the absence of allied radicals should also be described. Multistep procedures may be described schematically. Sample identification number, date(s) of experiment, page number of the laboratory note book etc. should be properly indexed keeping a space for observations/remarks etc. by the teacher.

9.12. Examples of Qualitative Analysis of Model Inorganic Samples

Example (9.5)

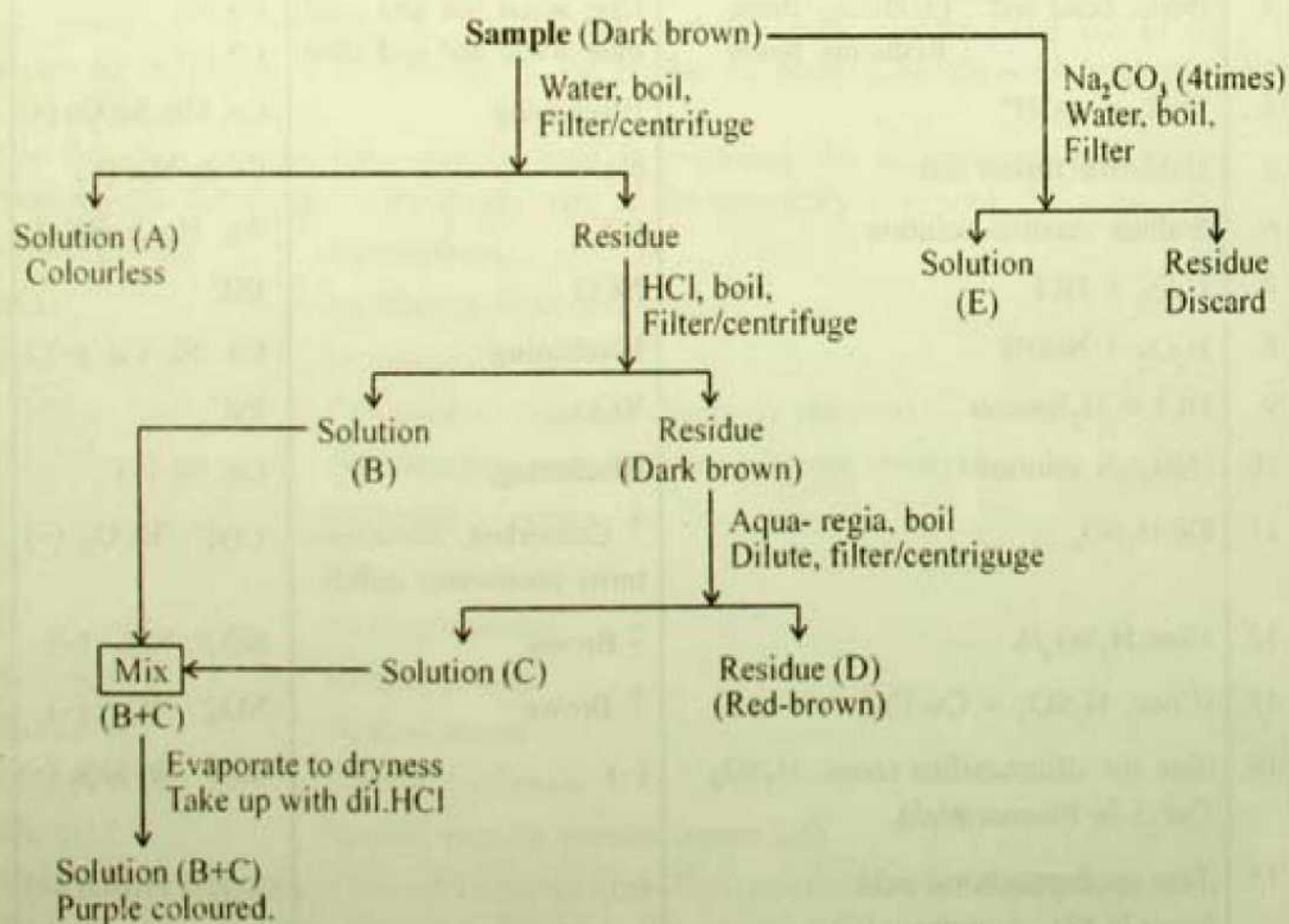
Date 02-08-2006	Sample No. 01	Colour Dark brown	Texture Amorphous powder
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1. Preliminary tests for cation and anion radicals with the solid sample

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Ignition test	Brown ↑	NO_3^- , NO_2^- (~)
2.	Flame test	Crimson flame	Sr, CaF_2 (~)
3.	Borax bead test : Oxidizing flame : Reducing flame	blue when hot and cold blue when hot and cold	Co (~) Co (~)
4.	" $\text{NH}_3 + \text{AgOH}$ "	Blackening	Co, Mn, Ni, Cu (~)
5.	Oxidative fusion test	(-)	Cr & Mn (x)
6.	Sodium stannite solution	(-)	Ag, Hg & Bi(x)
7.	$\text{H}_2\text{O}_2 + \text{HCl}$	NCO	INC
8.	$\text{H}_2\text{O}_2 + \text{NaOH}$	Blackening	Co, Ni, Cu, (~)
9.	$\text{HCl} + \text{H}_2\text{S}$ -water	NCO	INC
10.	$(\text{NH}_4)_2\text{S}$ solution	Blackening	Co, Ni (~)
11.	Dil. H_2SO_4	↑ Colourless, odourless, turns lime-water milkly	CO_3^{2-} , HCO_3^- (~)
12.	Conc. $\text{H}_2\text{SO}_4/\Delta$	↑ Brown	NO_3^- , NO_2^- (~)
13.	(Conc. $\text{H}_2\text{SO}_4 + \text{Cu-T}$)/ Δ	↑ Brown	NO_3^- , NO_2^- (~)
14.	Test for silicate/silica (conc. $\text{H}_2\text{SO}_4 + \text{CaF}_2$) in Pb-crucible/ Δ	(-)	SiO_3^{2-} & SiO_2 (x)
15.	Test for borate/boric acid (conc. $\text{H}_2\text{SO}_4 + \text{methanol}$)/ Δ	(-)	BO_3^{3-} , H_3BO_3 (x)

Sl No.	Experiments /Reagents	Observations	Inferences
16.	NaOH/ Δ	(-)	NH_4^+ (x)
17.	(NaOH + Zn-dust)/ Δ	$\uparrow$ (NH_3)	NO_3^- , NO_2^- , ($\checkmark$)
18.	(HCl + Zn-dust)/ Δ	(-)	S^{2-} (x)
19.	Iodine-azide test	(-)	S^{2-} , $\text{S}_2\text{O}_3^{2-}$ & SCN^- (x)
20.	Test for Nitrite: Salfanilic acid + α -Naphthylamine.	(-)	NO_2^- (x)
21.	Test-20 in presence of Zn-dust	(+)	NO_3^- (Cl.)
22.	Test for phosphate/arsenate: (HNO_3 extract + Ammonium molybdate)/ Δ	(-)	PO_4^{3-} & AsO_4^{3-} (x)

2. Preparation of solutions for wet tests



3. Tests for anions with the Na_2CO_3 extract (E)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Test for NO_3^- & NO_2^- (a) Sulfanilic acid + α -Naphthylamine (b) Reaction mixture of test 1(a) + Zn - dust	(-) (+) Red colouration	NO_2^- (x) NO_3^- (Cf)
2.	Ring test for NO_3^-	(+)	NO_3^- (Cf)
3.	HNO_3 + AgNO_3 solution	(-)	Halides (x)
4.	$(\text{HNO}_3 + (\text{NH}_4)_2\text{MoO}_4)/\Delta$	(-)	PO_4^{3-} & AsO_4^{3-} (x)
5.	Dil.HCl + BaCl_2 solution	(-)	SO_4^{2-} (x)
6.	HCl + FeCl_3 solution	(-)	SCN^- (x) $[\text{Fe}(\text{CN})_6]^{4-}$ (x)
7.	Dil. H_2SO_4 + FeSO_4 solution	(-)	$[\text{Fe}(\text{CN})_6]^{3-}$ (x)
8.	Sodium nitroprusside	(-)	S^{2-} (x)
9.	Zinc nitroprusside	(-)	SO_3^{2-} (x)
10.	HCl + H_2S - water	(-)	Thioformers (x)

4. Test for cations & anions with the aqueous extract (A)

Note: Since only the nitrate (NO_3^-) ion has been detected in the Na_2CO_3 extract (E), the other anions need not be searched in the aqueous extract (A).

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Evaporation to dryness	Residue left	Aqueous part (✓)
2.	Flame test with the residue of test (1)	(+) Crimson red flame	Sr. (✓)
3.	Litmus paper (red & blue)	Neutral	INC
4.	POS-reagent + NH_3 [Dil. ($\text{H}_3\text{PO}_4 + \text{H}_2\text{C}_2\text{O}_4 + \text{H}_2\text{SO}_4$) mixture]	↓	Gr(I-V) (✓)
5.	Dil.HCl	(-)	Gr-I (x)
6.	Dil.HCl + H_2S - water	(-)	Gr-II (x)
7.	$(\text{NH}_4\text{Cl} + \text{NH}_3)/\Delta$ gently	(-)	Gr-III A (x)
8.	Reaction mixture of test-7 + H_2S -water	(-)	Gr-III B (x)

Sl No.	Experiments /Reagents	Observations	Inferences
9.	$\text{NH}_4\text{Cl} + \text{NH}_3 + \text{saturated } (\text{NH}_4)_2\text{CO}_3$	↓ White	Gr-IV (✓)
10.	Flame test with the precipitate of test-9	(+) Crimson red flame	Sr^{2+} (Cf)
11.	Precipitation of Gr-IV (test-9) was completed by adding $(\text{NH}_4)_2\text{CO}_3$ as required and centrifuged. Centrifugate was evaporated to dryness, moistened with 1-2 drops of conc. HNO_3 and heated in a Fume Cupboard until white fumes ceased to appear. Cooled and taken up with ~0.5 ml of water and the extract was tested as follows: (i) $\text{NaH}_2\text{PO}_4 + \text{NH}_3$ (ii) Zn-uranylacetate (iii) Sodium cobaltinitrite test	(-) (-) (-)	Mg^{2+} (×) Na^+ (×) K^+ (×)

5. Confirmatory test for the radicals indicated in the aqueous extract (A)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	The white precipitate of Gr-VI carbonates obtained in test-9 of section 4, was dissolved in dil.2M acetic acid and the solution was tested as follows: (i) K_2CrO_4 solution (ii) Conc.solution of $(\text{NH}_4)_2\text{SO}_4$ (iii) Flame test with the precipitate of test-1(ii) after reduction. (iv) Sufficient $(\text{NH}_4)_2\text{SO}_4$ was added to the reaction mixture of test-1(ii) to complete the precipitation. Centrifuged and the centrifugate after concentration was treated with saturated ammonium oxalate and NH_3 until alkaline and warmed.	(-) ↓ White Crimson flame (-)	Ba^{2+} (×) Sr^{2+} (✓) Sr^{2+} (Cf) Ca^{2+} (×)

Sl No.	Experiments /Reagents	Observations	Inferences
2.	(i) Aq-extract (A) in a test tube + freshly prepared FeSO_4 solution. Centrifuged to remove SrSO_4 that precipitates and conc. H_2SO_4 was added to the centrifugate carefully down the side of the test tube. (ii) Diazo test : Aq-extract + sulfanilic acid + α -naphthylamine (iii) Diazo test 2(ii) in presence of Zn-dust.	Brown ring at the junction of the two liquids. (-) (+) Red colouration	NO_3^- (Cf) NO_2^- (x) NO_3^- (Cf)

Conclusion : Aqueous part (A) contains : Sr^{2+} and NO_3^- ions only. Therefore, $\text{Sr}(\text{NO}_3)_2$ is present.

6. Tests for cations with the HCl-extract (B + C)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Conc. HCl/Δ	Green colouration, turns purple on dilution with water	Co^{2+} (✓)
2.	H_2S - water	(-)	Gr-II (x)
3.	$(\text{NH}_4\text{Cl} + \text{NH}_3)/\Delta$	(-)	Gr-III A (x)
4.	Reaction mixture of test-3 + H_2S -water	↓ Black	Gr-III B (✓)
5.	Reaction mixture of test-4 after complete precipitation was centrifuged and the precipitate was subjected to the following tests. (i) Dil. HCl/Δ (boiled) (ii) $(\text{NaOCl} + \text{HCl})/\Delta$ (iii) Solution of test-5(ii) + NH_4SCN + Acetone (iv) Solution of test-5(ii) + $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]$ + ZnSO_4 solution, stirred (v) Solution test-5(ii) + $\text{DMGH}_2 + \text{NH}_3$	Does not dissolve Dissolved (+) Blue colouration ↓ Blue (-)	INC Co & Ni (~) Co^{2+} (Cf.) Co^{2+} (Cf) Ni^{2+} (x)
6.	Tests with the centrifugate of test-5. Evaporated to dryness, moistened with 1-2 drops of conc. HNO_3 , heated strongly inside a <i>Fume Chamber</i> until white fumes ceased.	No residue was left.	Gr-IV & V (x)

Conclusion: The HCl -extract (B + C) contains : Co^{2+} ion.

7. Identification of the insoluble residue (D)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Examination of colour.	Red-brown	$\sim \text{Fe}_2\text{O}_3$
2.	Flame test after reduction	(-)	BaSO_4 (x) SrSO_4 (x)
3.	Fusion with KHSO_4 , extratction of the fused mass with dil.1M H_2SO_4 and testing of the extract as follows: (i) NH_4SCN (ii) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (iii) Alizarin-S test	(+) Red colouration (+) Prussian blue colouration (-)	Fe^{3+} (Cf) Fe^{3+} (Cf) Al^{3+} (x)
4.	NH_4^+ -acetate extract + K_2CrO_4	(-)	PbSO_4 (x)

Conclusion : The insoluble residue is : Fe_2O_3

8. Probable composition of the mixture.

Radicals detected

	Cation/Compound	Anion/Compound
Aqueous extract :	Sr^{2+}	NO_3^-
HCl extract :	Co^{2+}	---
Na_2CO_3 - extract :	—	NO_3^-
Insoluble material :	Fe_2O_3	—

(1) Since the aqueous extract contained only Sr^{2+} and NO_3^- ions and was neutral to litmus, therefore, $\text{Sr}(\text{NO}_3)_2$ might be present in the mixture and it should not contain any soluble acidic or basic material (i.e., SrO or $\text{Sr}(\text{OH})_2$ etc.)

(2) The insoluble material was unambiguously Fe_2O_3 as it was red-brown in colour and did not contain Al_2O_3 . Silicates and silica were also absent. So were the sulfates of Ba and Sr as indicated from the negative observations of the flame test with the insoluble part. PbSO_4 was also found to be absent.

(3) Since the colour of the original sample and also of the residue after extraction with water were almost same, i.e dark brown, cobalt should not be present as its black coloured oxide. It could, however, exist as its ash coloured carbonate (CoCO_3). More over, carbonate was also indicatd in the preliminary test on the solid sample. The residue after HCl-extraction was red-brown, which was Fe_2O_3 . The colour change of the residue from dark brown to red-brown on HCl extraction might be due to dissolution of ash coloured CoCO_3 in HCl. Therefore, the CoCO_3 remained dissolved HCl soluble part.

(4) Thus, the probable composition of the mixture should be:

$\text{Sr}(\text{NO}_3)_2$	...	(aqueous extract)
CoCO_3	...	(HCl - extract)
Fe_2O_3	...	Insoluble part

9. Tests to be described:

- Borax bead test for Co,
- Flame test for Sr^{2+} ,
- Ring test for NO_3^- (aq-extract and Na_2CO_3 - extract),
- Analysis of Group-IV precipitate for Sr^{2+} (aqueous extract),
- Analysis of Group-IIIB (HCl-extract) for Co^{2+} ,
- KHSO_4 fusion and test of Fe^{3+} in the fusion extract of the insoluble part.

Example (9.6)

Date 01.12.2006	Sample No. 02	Colour White	Texture Crystalline
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1. Preliminary tests on the solid sample

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Ignition test	Melting occurs $\uparrow$ (Violet)	Na^+ , K^+ (~) I^- (~)
2.	Flame test : Naked eye Double blue glass	Violet flame Red flame	K^+ (~) K^+ ($\checkmark$)
3.	Borax bead test	(-)	Transition elements ($\times$)
4.	Oxidative fusion test	(-)	Cr, & Mn ($\times$)
5.	Aq- NH_3	(-)	INC
6.	(i) Dil.HCl (ii) Dil.HCl + Starch solution	Brown colouration Blue colouration	Br^- , I^- & oxidant I^- & oxidant
7.	Conc. $\text{H}_2\text{SO}_4/\Delta$	$\uparrow$ Violet	I^- ($\checkmark$)
8.	(Conc. H_2SO_4 + MnO_2)/ Δ	$\uparrow$ Violet	I^- ($\checkmark$)
9.	NaOH/Δ	(-)	NH_4^+ ($\times$)
10.	(NaOH + Zn-dust)/ Δ	(-)	NO_2^- & NO_3^- ($\times$)

2. Preparation of solution for wet tests

Sample was completely soluble in cold water. The following tests were performed with the aqueous solution of the sample.

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Examination of colour	Colourless	Transition metal (×)
2.	Litmus paper (blue & red)	No. change of colour	Neutral
3.	Na_2HPO_4 solution Note: Absence of NH_4^+ was indicted in earlier tests –1(9).	No precipitate	(i) Gr.I to Gr-IV & Mg (×) (ii) Na^+ & K^+ (~)
4.	Zincuranyl acetate test	(–)	Na^+ (×)
5.	Sodium cobaltinitrite test	(+)	K^+ (✓) ($\therefore \text{NH}_4^+$ absent)
6.	Dil.HCl	Brown colouration	Br^- , I^- and oxidant (✓)
7.	CHCl_3 was added to reaction mixture of test-6 and shaken.	Violet organic layer	I^- (Cf)
8.	Cl_2 -water was added to the reaction mixture of test-7 and shaken.	Violet organic layer	I^- (Cf)
9.	Violet organic layer was removed from the test solution with the aid of a capillary dropper and Cl_2 -water was added in excess and shaken with CHCl_3 .	Disappearance of the violet colour of the organic layer and appearance of yellow brown colour.	Br^- (✓)
10.	$\text{HNO}_3 + \text{AgNO}_3$	↓ yellow	Halides specially I^- , halate,
11.	Separation of halide and halate mixture (cf. Sect. 7.4)	(+)	Br^- , I^- and BrO_3^- (✓)

Therefore, the aqueous solution of the sample contains : K^+ ion as the only cation along with Br^- , BrO_3^- and I^- anions.

3. Probable Composition

(i) Sample was completely soluble in water.

(ii) All the four radicals, K^+ , BrO_3^- , Br^- and I^- were detected in the aqueous solution of the sample. So, the probable composition of the mixture should be: KBr , KBrO_3 , KI .

Aqueous solution of the sample was neutral, because, $K^+(aq)$ has no acidic property and the anions BrO_3^- , Br^- and I^- are all derived from strong acids. Therefore, all these three anions are weak bases and do not hydrolyze in aqueous solution to make it alkaline.

Brown colouration of the aqueous solution on acidification was due to oxidation of Br^- and I^- by BrO_3^- ion to set free Br_2 and I_2 .

4. Tests to be described:

- Flame test for K^+ ion,
- Sodium cobaltinitrite test for K^+ ion (confirmatory test),
- Separation of Br^- , I^- and BrO_3^- and detection of individual anion radicals,
- Confirmatory tests for Br^- , I^- and BrO_3^- ions.

Example (9.7)

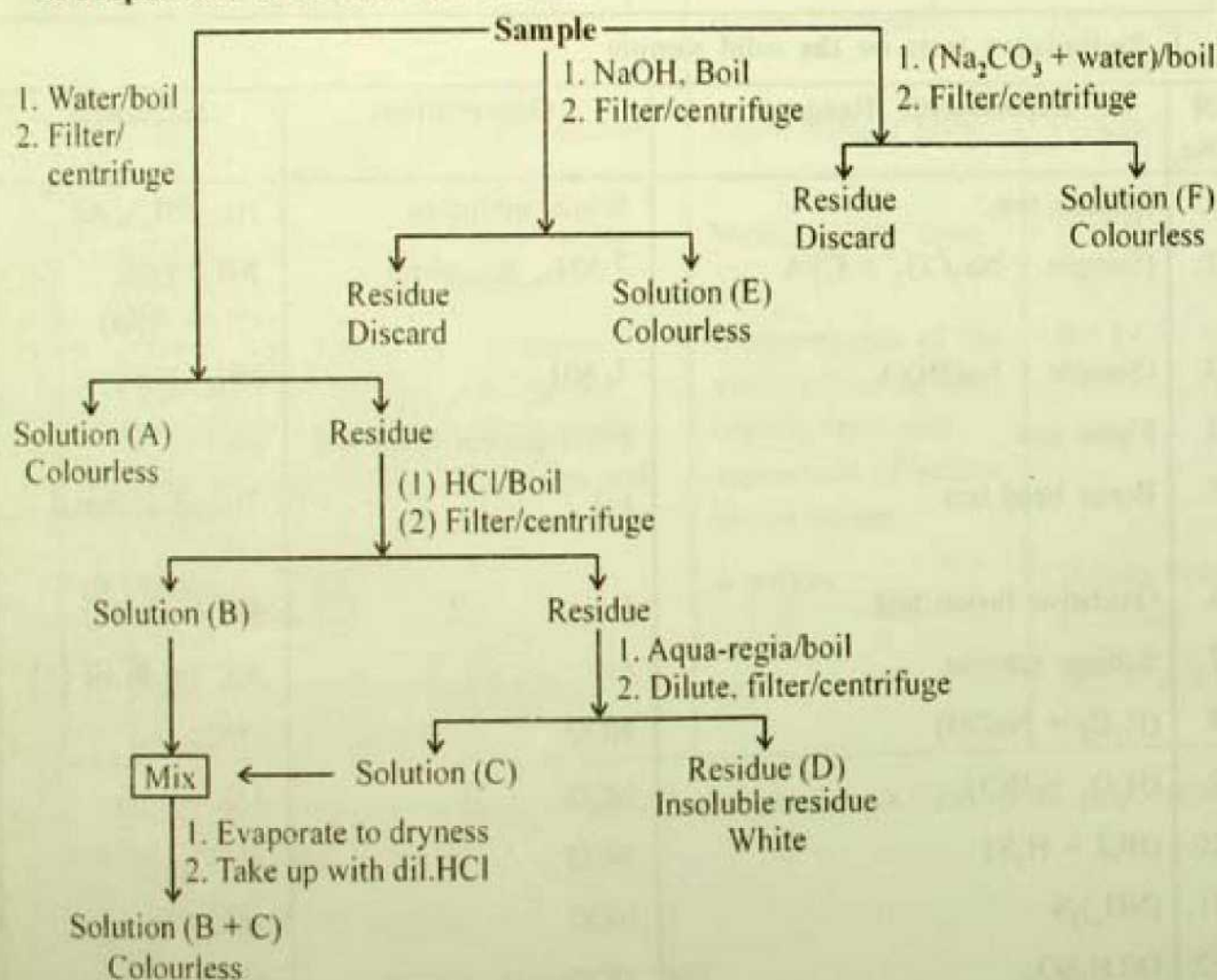
Date 05.12.2006	Sample No. 03	Colour White	Texture Mixture of crystalline and amorphous powder
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1. Preliminary tests on the solid sample

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Ignition test.	White sublimate	Hg, NH_4^+ , As
2.	(Sample + Na_2CO_3 + C)/ Δ	$\uparrow NH_3$, No mirror	NH_4^+ ($\checkmark$), Hg & As(x)
3.	(Sample + NaOH)/ Δ	$\uparrow NH_3$	NH_4^+ (Cf.)
4.	Flame test	(+) Transient brick red	Ca (~)
5.	Borax bead test	(-)	Transition metal (x)
6.	Oxidative fusion test	(-)	Mn & Cr (x)
7.	Sodium stannite	(-)	Ag, Hg & Bi (x)
8.	(H_2O_2 + NaOH)	NCO	INC
9.	(H_2O_2 + HCl)	NCO	INC
10.	(HCl + H_2S)	NCO	INC
11.	$(NH_4)_2S$	NCO	INC
12.	Dil. H_2SO_4	NCO	INC
13.	Conc. H_2SO_4/Δ	NCO	INC
14.	(Conc. H_2SO_4 + MnO_2)/ Δ	(-)	Cl^- , Br^- & I^- (x)

Sl No.	Experiments /Reagents	Observations	Inferences
15.	(Conc. H_2SO_4 + Cu-T)/ Δ	(-)	NO_2^- & NO_3^- (x)
16.	Test for borate/ H_3BO_3	(-)	BO_3^- & H_3BO_3 (x)
17.	I_2 -azide test	(-)	S^{2-} , $\text{S}_2\text{O}_3^{2-}$ & SCN^- (x)
18.	Reductive fusion test for SO_4^{2-}	(-)	SO_4^{2-} (x)
19.	Test for SiO_3^{2-} & SiO_2	(-)	SiO_3^{2-} & SiO_2 (x)
20.	(Sample + conc. HNO_3 + $(\text{NH}_4)_2\text{MoO}_4$ solution)/ Δ	Yellow mass	PO_4^{3-} , AsO_4^{3-} (~)

2. Preparation of solution for wet tests



3. Tests for anions in the Na_2CO_3 -extract (F)

Na_2CO_3 extract was neutralized with dil. HNO_3 , CO_2 was boiled off, rendered slightly alkaline with very dilute NH_3 , then boiled to remove excess NH_3 . The resulting neutralized

Na_2CO_3 extract was treated with a concentrated solution of $\text{Zn}(\text{NO}_3)_2$, warmed gently, when a white precipitate appeared. The precipitate was filtered/centrifuged. The following tests were carried out on the precipitate (X) and the solution (Y)*.

3(a) Tests for anions on the precipitate (X)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Acetic acid + Pb-acetate	↓ White	INC
2.	Dil- H_2SO_4 + FeSO_4 solution	(-)	$[\text{Fe}(\text{CN})_6]^{3-}$ (×)
3.	Dil.HCl + FeCl_3 solution	(-)	$[\text{Fe}(\text{CN})_6]^{4-}$ (×)
4.	(HNO_3 + $(\text{NH}_4)_2\text{MoO}_4$ solution)/ Δ	↓ Canary yellow	PO_4^{3-} , AsO_4^{3-} (✓)
5.	(Canary yellow precipitate of test-4 + tartaric acid)/boiled	Precipitate remained undissolved	PO_4^{3-} (✓)
6.	Precipitate (X) was dissolved in dil. HCl, treated with magnesia mixture, rendered ammoniacal and warmed.	↓ White crystalline	PO_4^{3-} , AsO_4^{3-} (✓)
7.	Precipitate of test-6 + starch-KI + dil.HCl	(-)	AsO_4^{3-} (×)
8.	BaCl_2 solution + Zr-alizarin solution + dil.HCl	(-)	F^- (×)

* **Note:** Test for NO_3^- ion, if suspected in the preliminary tests, should be carried out on the original Na_2CO_3 extract before treating with dil. HNO_3 or $\text{Zn}(\text{NO}_3)_2$ etc.

3.(b) Tests for anions in the solution (Y)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	I_2 -azide test on (Y)	(-)	SCN^- , S^{2-} , $\text{S}_2\text{O}_3^{2-}$ (×)
2.	(Y + dil. HNO_3)/boiled off CO_2 + $\text{Ba}(\text{NO}_3)_2$ solution	(-) No ↓	SO_4^{2-} (×)
3.	Y + Cl_2 -water + fuchsin-bisulfate	(-)	Br^- (×)
4.	(Y + dil. HNO_3)/boiled off CO_2 + AgNO_3	(-)	Cl^- , Bi^- & I^- (×)

4. Tests for cations in the aqueous extract (A)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Colour	Colourless	INC
2.	Litmus paper (red & blue)	Blue to red	Weakly acidic
3.	Evaporated to dryness	Residue left	Aq-part (✓)
4.	($\text{Na}_2\text{HPO}_4 + \text{NH}_3$)	(-) No precipitate	NH_4^+ , K^+ , Na^+ (-)
5.	(Conc. $\text{HNO}_3 + (\text{NH}_4)_2\text{MoO}_4$)/ Δ	↓ Canary yellow	PO_4^{3-} , AsO_4^{3-} (✓)
6.	(Canary yellow precipitate of test-5 + tartaric acid)/boiled	Precipitate does not dissolve	PO_4^{3-} (Cf)
7.	(Magnesia mixture + NH_3)/warm	↓ White crystalline	PO_4^{3-} , AsO_4^{3-} (✓)
8.	Precipitate of test-7 + starch-KI + dil.HCl	(-) No blue colouration	AsO_4^{3-} (×)
9.	Sodium cobaltinitrite test	(+)	K^+ , NH_4^+ (~)
10.	Sodium cobaltinitrite test after removing NH_3 completely by boiling with NaOH solution	(-)	NH_4^+ (✓), K^+ (×)
11.	Issuing gas of test-10 was tested with: (i) Nessler's reagent paper (ii) Phenolphthalin paper	(+) Brown spot (+) Red spot, disappears on drying	NH_4^+ (Cf.) NH_4^+ (Cf.)
12.	Zincuranyl acetate test	(-)	Na^+ (×)

Therefore, the aqueous extract (A) contained : NH_4^+ and PO_4^{3-} ions.

5. Tests for cations in the HCl extract (B + C)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Colour	Colourless	INC
2.	Evaporated to dryness	Residue left	HCl part (✓)
3.	($\text{HNO}_3 + (\text{NH}_4)_2\text{MoO}_4$)/ Δ	↓ Canary yellow	PO_4^{3-} , AsO_4^{3-} (✓)
4.	($\text{HNO}_3 + (\text{NH}_4)_2\text{MoO}_4 + \text{tartaric acid}$)/ Δ	↓ Canary yellow	PO_4^{3-} (Cf.)
5.	H_2S -water	(-)	Gr-I to Gr-II (×)

Sl No.	Experiments /Reagents	Observations	Inferences
6.	Phosphate was removed by Pb-acetate method. Excess Pb^{2+} was separated as PbS by adding H_2S -water. Excess H_2S was boiled off. Oxidized with conc. HNO_3 and was treated with $NH_4Cl + aq-NH_3$ until ammoniacal.	(-) No ↓	Gr-IIIA (x)
7.	Resulting solution of test-6 was divided into 2-parts and tested as follows: (i) Smaller part + H_2S -water (ii) Larger part + saturated $(NH_4)_2CO_3$	(-) No ↓ ↓ White	Gr-IIIB (x) Gr-IV (✓)
8.	Flame test with the white precipitate of test 7(ii)	(+) Transient brick red	Ca^{2+} (✓)
9.	White precipitate of test-7(ii) was dissolved in dil.2M acetic acid, the resulting solution was divided into three parts and tested as follows: Part-(i) K_2CrO_4 solution was added Part-(ii) Saturated $(NH_4)_2SO_4$ solution was added Part-(iii) Saturated ammonium oxalate solution was added and the solution was made alkaline with $aq-NH_3$.	(-) (-) ↓ White crystalline	Ba^{2+} (x) Sr^{2+} (x) Ca^{2+} (Cf)
10.	Flame test with the residue of test 9(iii)	Transient brick red flame	Ca^{2+} (Cf)

∴ HCl soluble part contained : Ca^{2+} and PO_4^{3-} ions.

6. Tests for radicals in the NaOH extract (E)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Alizarin-S test for aluminium after removing phosphate as Ba-phosphate	(+) Red lake	Al^{3+} (✓) (Cf.)
2.	Mercuriothiocyanate test for Zn^{2+} : (i) With $CuSO_4$ (ii) With $CoSO_4$	(-) (-)	Zn^{2+} (x) Zn^{2+} (x)
3.	$(HNO_3 + (NH_4)_2MoO_4 + \text{tartaric acid})/\Delta$	↓ Canary yellow	PO_4^{3-} (✓)

Therefore, the NaOH extract contained : Al^{3+} ion and PO_4^{3-} ion.

7. Identification of the insoluble residue (D)

Sl No.	Experiments /Reagents	Observations	Inferences
1.	Colour	White	INC
2.	Flame test after reduction	(-)	BaSO ₄ , SrSO ₄ (×)
3.	Luminescence test for SnO ₂	(-)	SnO ₂ (×)
4.	Fusion with Na ₂ CO ₃ bead on platinum wire loop, + HNO ₃ + (NH ₄) ₂ MoO ₄ + benzidine + NH ₄ ⁺ -acetate (solid). (Test for SiO ₃ ²⁻ /SiO ₂)	(-)	SiO ₃ ²⁻ & SiO ₂ (×)
5.	(D + ammonium acetate solution)/boiled, centrifuged. The centrifugate was treated with: (i) K ₂ CrO ₄ solution (ii) KI solution	(-) (-)	PbSO ₄ (×) PbSO ₄ (×)
6.	Fused with KHSO ₄ , extracted with dil.H ₂ SO ₄ . Extract after neutralization with NH ₃ , was subjected to alizarin-S test.	(+) Red lake	Al ₂ O ₃ (Cf.)
7.	(i) Fused with Na ₂ CO ₃ bead on a platinum wire loop, extracted with water and the extract was boiled with some NH ₄ Cl (solid). (ii) The precipitate of test 7(i) was washed free from alkali and was subjected to alizarin-S test	↓ Gelatinous white (+) Red lake	Al ₂ O ₃ (✓) Al ₂ O ₃ (Cf)

Therefore, the white insoluble residue (D) was Al₂O₃.

8. Probable composition

Radicals detected

	Cations	Anions
Aqueous extract (A) :	NH ₄ ⁺	PO ₄ ³⁻
Na ₂ CO ₃ extract (F) :	—	PO ₄ ³⁻
NaOH extract (E) :	Al ³⁺	PO ₄ ³⁻
Acid extract (B+C) :	Ca ²⁺	PO ₄ ³⁻
Insoluble part (D) :	Al ₂ O ₃	—

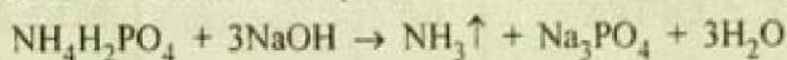
(i) Since the both NH_4^+ and PO_4^{3-} ions were detected in the aqueous extract, and since the aqueous extract was faintly acidic, these ions might be present as $\text{NH}_4\text{H}_2\text{PO}_4$ or $(\text{NH}_4)_2\text{HPO}_4$. The former salt, $\text{NH}_4\text{H}_2\text{PO}_4$ was more likely, since HPO_4^{2-} ion would render the aqueous solution slightly alkaline, so that weakly acidic NH_4^+ ion would deprotonate to liberate NH_3 gas, which was, however not observed.

(ii) Ca^{2+} and PO_4^{3-} ions were detected in the acid extract (B+C). These ions could occur as $\text{Ca}_3(\text{PO}_4)_2$, or, CaHPO_4 .

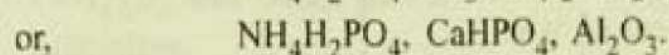
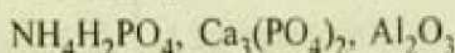
(iii) The insoluble residue (D) was unambiguously Al_2O_3 .

(iv) Al^{3+} and PO_4^{3-} ions were detected in the NaOH extract (E). But since Al^{3+} was not found in the acid extract (B+C), therefore, AlPO_4 was unlikely to occur.

(v) Al^{3+} was found as Al_2O_3 . Because of its amphoteric nature, Al_2O_3 might have dissolved in the NaOH solution, forming aluminate (AlO_2^-) ion. PO_4^{3-} ion possibly came into this solution due to the acid-base cum double decomposition reaction between $\text{NH}_4\text{H}_2\text{PO}_4$ and NaOH:



(vi) Therefore, the most probable composition of the mixture should be:



9. Tests to be described

(i) NH_4^+ : Preliminary tests (1, 2, 3), Cobaltinitrite test.

(ii) Ca^{2+} : Flame test, wet test (Gr-IV), flame test with Gr-IV precipitate.

(iii) PO_4^{3-} : Ammonium molybdate tests, magnesia mixture test, separation from arsenate arsenite and confirmation.

(iv) Al_2O_3 : Alizarin red-S test with NaOH extract (E), Na_2CO_3 -fusion exact and KHSO_4 fusion extract of the insoluble part (D).

Example (9.8)

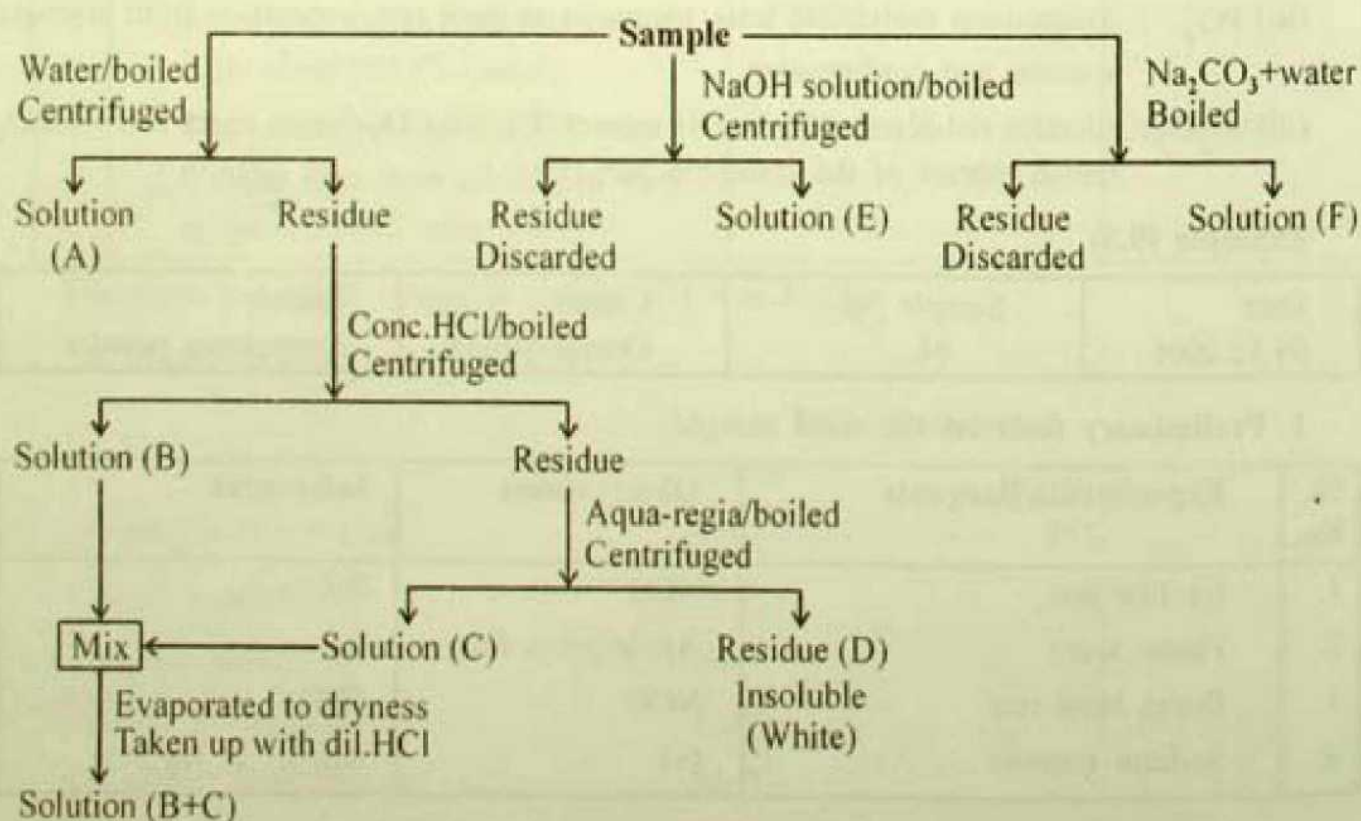
Date	Sample No.	Colour	Texture
04.12.2006	04	Orange-yellow	Amorphous powder

1. Preliminary tests on the solid sample

Sl. No.	Experiments/Reagents	Observations	Inferences
1.	Ignition test	NCO	INC
2.	Flame test	Apple-green flame	Ba
3.	Borax bead test	NCO	INC
4.	Sodium stannite	(-)	Ag, Bi & Hg (x)

Sl. No.	Experiments/Reagents	Observations	Inferences
5.	Oxidative fusion test	(-)	Cr & Mn (×)
6.	(H ₂ O ₂ + NaOH)	NCO	INC
7.	(H ₂ O ₂ + HCl)	NCO	INC
8.	(HCl + H ₂ S)	NCO	INC
9.	(NH ₄) ₂ S _r	Orange yellow part dissolves	Gr-IIB (~)
10.	Dil.H ₂ SO ₄	NCO	INC
11.	Conc.H ₂ SO ₄ /Δ	Smell of burning sulfur	S ²⁻ , S ₂ O ₃ ²⁻ (~)
12.	(Conc. H ₂ SO ₄ + MnO ₂)/Δ	(-)	Cl ⁻ , Br ⁻ , I ⁻ (×)
13.	(Conc. H ₂ SO ₄ + Cu-T)/Δ	(-)	NO ₂ ⁻ , NO ₃ ⁻ (×)
14.	Test for BO ₃ ³⁻ & H ₃ BO ₃	(-)	BO ₃ ³⁻ & H ₃ BO ₃ (×)
15.	I ₂ - azide test	(+) Discharge of I ₂ colour with effervescence	S ²⁻ , S ₂ O ₃ ²⁻ SCN ⁻ , (✓)
16.	(Zn+HCl)/warming	↑(H ₂ S), Pb-acetate paper turned black	S ²⁻ (✓)

2. Preparation of solutions of wet tests



3. Test with aqueous extract (A)

Sl. No.	Experiments/Reagents	Observations	Inferences
1.	Colour	Colourless	INC
2.	Evaporated to dryness	Residue left	Aqueous part (✓)
3.	Litmus papers (red & blue)	Red turned blue	alkaline
4.	Na_2HPO_4 solution	↓ White	Gr (I-V) (✓)
5.	Dil.HCl	↓ Orange	Gr-II B (✓)
6.	Remaining part of solution (A) + sufficient dil.HCl to completely precipitate the orange compound, centrifuged, and the precipitate was washed with dil.HCl. The following tests were performed with the orange precipitate.		Sb sulfide (~)
	(i) $(\text{NH}_4)_2\text{S}_x$ was added to the precipitate.	Precipitate dissolved	Gr-II B (✓)
	(ii) Precipitate was digested with conc.HCl	Precipitate dissolved	As(x), Sb & Sn (~)
	(iii) Solution from test 6(ii)+ NH_3 until just neutral+oxalic acid + H_2S water	↓ Orange	Sb (✓)
	(iv) (Solution from test 6 (ii) + NaNO_2) + rhodamine-B	Violet colouration	Sb (Cf)
	(v) Solution from test 6(ii) + iron-nail, warmed, centrifuged and the centrifugate was treated with HgCl_2 solution.	(-)	Sn (x)
	(vi) Precipitate of test-5 or 6 + Zn dust + HCl.	↑ H_2S , turned lead acetate paper black	S^{2-} (Cf.)
7.	Tests with the centrifugate from test-6. The centrifugate was boiled to expel H_2S , concentrated to a small volume, oxidized by boiling with a few drops of conc. HNO_3 , divided into several parts and the following tests were performed.		

Sl. No.	Experiments/Reagents	Observations	Inferences
7.	(a) Evaporated to dryness (b) Diluted with water + H_2S -water (c) $(HNO_3 + (NH_4)_2MoO_4)/\Delta$ (d) $(NH_4Cl + NH_3)/boil$ (e) $(NH_4Cl + NH_3 + H_2S - water)$ (f) $NH_4Cl + NH_3 + saturated (NH_4)_2CO_3$. Centrifuged and the following test were performed: (i) Flame test on the white precipitate of test 7(f) (ii) White precipitate of test 7(f) was dissolved in 2M acetic acid and was treated with K_2CrO_4 solution. (iii) Solution of test 7(f)(ii) was treated with sufficient K_2CrO_4 to precipitate $BaCrO_4$ completely, centrifuged, the centrifugate was made alkaline with NH_3 and treated with saturated $(NH_4)_2CO_3$ solution. (iv) Centrifugate of test-7(f) was evaporated to dry ness, moistened with drops of conc. HNO_3 and heated strongly inside a (Fume Cupboard).	Residue left (-) (-) (-) (-) ↓ White Apple-green flame ↓ Yellow ($BaCrO_4$) No precipitate No residue left	Radicals (✓) Gr-II (×) PO_4^{3-} (×) Gr-IIIA (×) Gr-IIIB (×) Gr-IV (✓) Ba (✓) Ba (Cf.) Sr & Ca (×) Gr-V (×)

Therefore, the aqueous extract (A) contained: Sb^{3+} , S^{2-} and Ba^{2+} ions.

4. Tests with the Na_2CO_3 -extract (F)

Sl. No.	Experiments/Reagents	Observations	Inferences
1.	Colour	Colourless	INC
2.	(a) When dil. HNO_3 was added to (F) for neutralization and removal of CO_2 , an orange yellow precipitate appeared.	↓ Orange yellow	(~) Sulfides of thioformers, As, Sb, Sn

Sl. No.	Experiments/Reagents	Observations	Inferences
	(b) Sufficient dilute HNO_3 was added to completely separate the orange yellow compound by precipitation. The mixture was centrifuged, the precipitate was boiled with conc. HCl . (c) Rhodamine-B test with the HCl solution of the orange precipitate of test 2(b) after oxidation with NaNO_2 . (d) HCl solution of the orange precipitate of tests 2(b) after reduction with iron nails, was treated with HgCl_2 solution.	Precipitate dissolved (+) Violet colouration (-)	As-sulfide ($\times$) Sb-Sn-sulfide ($\checkmark$) Sb (Cf) Sn ($\times$)
3.	Centrifugate from test 2(b) was boiled to expel H_2S , made just alkaline with NH_3 , boiled to expel excess NH_3 . The resulting neutral Na_2CO_3 - extract, was treated with an excess of saturated $\text{Zn}(\text{NO}_3)_2$ solution. Note: Since S^{2-} was removed from the test solution before addition of Zn-nitrate, precipitation of ZnS could not be observed at this stage.	No precipitate	Absence of AsO_4^{3-} , AsO_3^{3-} , PO_4^{3-} , $[\text{Fe}(\text{CN})_6]^{4-}$, $[\text{Fe}(\text{CN})_6]^{3-}$ BO_3^{3-} , F^- and S^{2-} .
4.	The following tests were performed with the resulting solution from test 3. (i) $\text{Dil.HNO}_3 + \text{AgNO}_3$ solution. (ii) $\text{Dil.HCl} + \text{BaCl}_2$ solution (iii) Solution from test 4(ii) + Br_2 -water (iv) $\text{Dil.HCl} + \text{FeCl}_3$ solution (v) Diazo test	(-) (-) (-) (-) (-)	Cl^- , Br^- , I^- ($\times$) BrO_3^- & IO_3^- ($\times$) SO_4^{2-} ($\times$) SO_3^{2-} ($\times$) SCN^- ($\times$) NO_2^- ($\times$)
5.	Na_2CO_3 extract (F) + sodium nitroprusside	Violet colouration	S^{2-} (Cf)
6.	Ring test for NO_3^- on Na_2CO_3 extract (F)	(-)	NO_3^- ($\times$)

Therefore, the Na_2CO_3 -extract (F) contained: S^{2-} and Sb^{3+} ions.

5. Tests with the NaOH extract (E)

Sl. No.	Experiments/Reagents	Observations	Inferences
1.	Acidification	↓ Orange yellow	Sb_2S_3 (~)
2.	The precipitate of test-1 was boiled with conc.HCl.	Precipitate dissolved	As_2S_3 (×) Sb_2S_3 , SnS (~)
3.	Rhodamine-B test with the solution from test-2 after oxidation with NaNO_2 .	(+)Violet colouration	Sb (Cf)
4.	Na-nitroprusside added to E.	(+) Violet colouration	S^{2-} (Cf.)
5.	Solution from test-2, reduced with iron nail and treated with HgCl_2 solution.	(-)	Sn (×)

Therefore, the NaOH extract (E) contained Sb^{3+} and S^{2-} ions.

6. Tests with the acid extract (B + C)

Sl. No.	Experiments/Reagents	Observations	Inferences
1.	Colour	Colourless	INC
2.	Evaporated to dryness	Residue left	Radicals (✓)
3.	$(\text{Na}_2\text{HPO}_4 + \text{NH}_3)$ until alkaline.	↓ White	Gr-I to IV, Mg (~)
4.	H_2S -water. Sufficient H_2S was added to complete the precipitation and centrifuged.	↓ Orange yellow, soluble in $(\text{NH}_4)_2\text{S}_x$	Gr-II B (✓)
5.	Precipitate from test-4, was subjected Gr-II B analysis: (i) (Precipitate + conc.HCl)/Δ (ii) Rhodamine-B test with the solution from test 5(i) after oxidation with NaNO_2 . (iii) Solution from test 5(i) was reduced with iron nails, centrifuged and the centrifugate was treated with HgCl_2 solution.	The precipitate dissolved completely (+) Violet colouration (-)	As (×) Sb , & Sn (~) Sb (Cf) Sn (×)
6.	1 drop of the centrifugate from test-5 was evaporated to dryness.	Residue left.	Gr-(III-V) radicals (✓)

Sl. No.	Experiments/Reagents	Observations	Inferences
7.	The main bulk of the centrifugate of test-5 was boiled to expel H_2S completely. Concentrated to a small volume, oxidized with conc.HNO_3 and the resulting solution was subjected to the following tests. (a) $(NH_4)_2MoO_4/\Delta$ (b) $(NH_4Cl + NH_3$ until alkaline)/boil (c) 1 drop of the resulting solution from test 7(b) + H_2S - water (d) 1 drop of the resulting solution from test 7(b) + saturated $(NH_4)_2CO_3$ solution. (e) Main bulk of resulting solution from test 7(b) + sufficient saturated $(NH_4)_2CO_3$ solution until precipitation was complete, centrifuged. The precipitate was subjected to Gr-IV analysis: (i) Precipitate from test-7(e) was subjected to flame test. (ii) Precipitate from test-7(e) was dissolved in 2M acetic acid and the solution was treated with K_2CrO_4 solution. (iii) Flame test with the yellow precipitate of test 7(e) (ii). (iv) Centrifugate of test 7(e)(ii) rendered alkaline with NH_3 and treated with saturated $(NH_4)_2CO_3$ solution. (f) The centrifugate from test 7(e) was evaporated to dryness, moistened with 1-2 drops of conc.HNO_3 and heated strongly inside a Fume Cupboard	(-) (-) (-) ↓ white Apple-green flame ↓ Yellow ($BaCrO_4$) Apple-green flame (-) No residue left	PO_4^{3-} (×) Gr-III A (×) Gr-III B (×) Gr-IV (✓) Ba (✓) Ba (Cf) Ba (Cf) Sr & Ca (×) Gr-V (×)

Therefore, the acid soluble part (B + C) contained : Sb^{3+} and Ba^{2+} ions.

7. Identification of the insoluble residue (D)

Sl. No.	Experiments/Reagents	Observations	Inferences
1.	Colour	White	INC
2.	Texture	Granular	SiO_2 (~)
3.	Flame test	(-)	BaSO_4 & SrSO_4 (x)
4.	Luminescence test	(-)	SnO_2 (x)
5.	Extraction with ammonium acetate + K_2CrO_4 solution	(-)	PbSO_4 (x)
6.	Fused with Na_2CO_3 bead on a platinum wire loop, extracted with water, and the extract was divided into two parts and tested as follows: Part-I : Alizarin-S test Part-II : HNO_3 + $(\text{NH}_4)\text{MoO}_4$ + benzidine + ammonium acetate (Benzidine blue-molybdenum blue test). Compared with a blank.	(-) (+) Blue colouration	Al_2O_3 (x) SiO_2 (Cf)

Therefore, the insoluble residue was SiO_2 .

8. Probable composition

Sample Part	Radicals detected		
	Cation	Anion	Compound
Aqueous extract (A)	Sb^{3+} , Ba^{2+}	S^{2-} ,	-
Acid extract (B+C)	Sb^{3+} , Ba^{2+}	-	-
NaOH extract (E)	Sb^{3+}	S^{2-}	-
Na_2CO_3 extract (F)	Sb^{3+}	S^{2-}	-
Insoluble residue (D)	-	-	SiO_2

(1) Since the aqueous solution was strongly alkaline, barium could be present as barium oxide (BaO) or hydroxide $\text{Ba}(\text{OH})_2$. Aqueous extract on acidification gave orange precipitate of Sb_2S_3 . In the alkaline aqueous extract, Sb_2S_3 dissolved in the form of oxy-, thio-, or, oxythio-salts, SbO_2^- or SbS_2^- and reappeared as Sb_2S_5 and Sb_2S_3 on acidification. The same phenomenon occurred on acidification of the NaOH extract (E) and the Na_2CO_3 extract (F). These suggested the presence of orange coloured Sb_2S_3 . This was also supported by the orange-yellow colour of the original sample.

(2) Presence of barium as BaS was ruled out, since it was dirty brownish coloured, whereas, the sample was orange-yellow coloured.

(3) No anion radical other than the S^{2-} ion was detected in the Na_2CO_3 extract. This also suggested the presence of barium as its oxide or, hydroxide, which produced strongly alkaline aqueous extract.

(4) The insoluble residue (D) was unambiguously SiO_2 .

(5) Therefore, the most probable composition of the mixture should be:

Sb_2S_3 , BaO (or $Ba(OH)_2$), SiO_2 .

Note: Alkaline nature of the aqueous extract and appearance of yellow to orange coloured precipitate on acidification of the aqueous extract, NaOH extract and Na_2CO_3 extract indicate the presence of sulfides of As, Sb and Sn (i.e., Group-IIB) (and also vanadium, molybdenum and tungsten sulfides)*. Whenever such unusual precipitate appears, it is convenient to complete the precipitation of the compound by adding sufficient amount of dilute acid (HCl or HNO_3 as the case may be) and to filter/centrifuge off the precipitate. The precipitate may be subjected to Gr-IIB analysis or individual tests may be carried out for the Gr-IIB cations. The filtrate/centrifugate after boiling off H_2S completely, may be subjected to Group-separation from Group-III A to Gr-V as usual, or, may be tested for cations by individual tests.

9. Tests to be described

- (i) Ba^{2+} ... Flame test on sample and on Gr-IV precipitate, Gr-IV analysis, sodium rhodizonate test.
- (ii) Sb (III)... Gr-IIB analysis, Rhodamine-B test.
- (iii) S^{2-} ... Preliminary test (16) with sample, precipitates from NaOH and Na_2CO_3 extracts, sodium nitroprusside and lead acetate paper tests.
- (iv) SiO_2 ... SiF_4 test, SiF_4 -molybdenum blue-benzidine blue test with original sample and insoluble residue.

Example (9.9)

Date: 07.11.2006

Sample No. 05

Sample containing six radicals including, two rare elements (for P.G. classes)*

1. Examination of physical characters

- (a) Colour : White powder with pale greenish yellow glow.
- (b) Texture : Partly amorphous partly crystalline.
- (c) Solubility : Partly soluble in water, partly in dilute HCl and partly insoluble.
 - (i) Colour of the aqueous extract : Pale greenish yellow.
 - (ii) Acid-base nature of the aqueous extract: Weakly acidic.

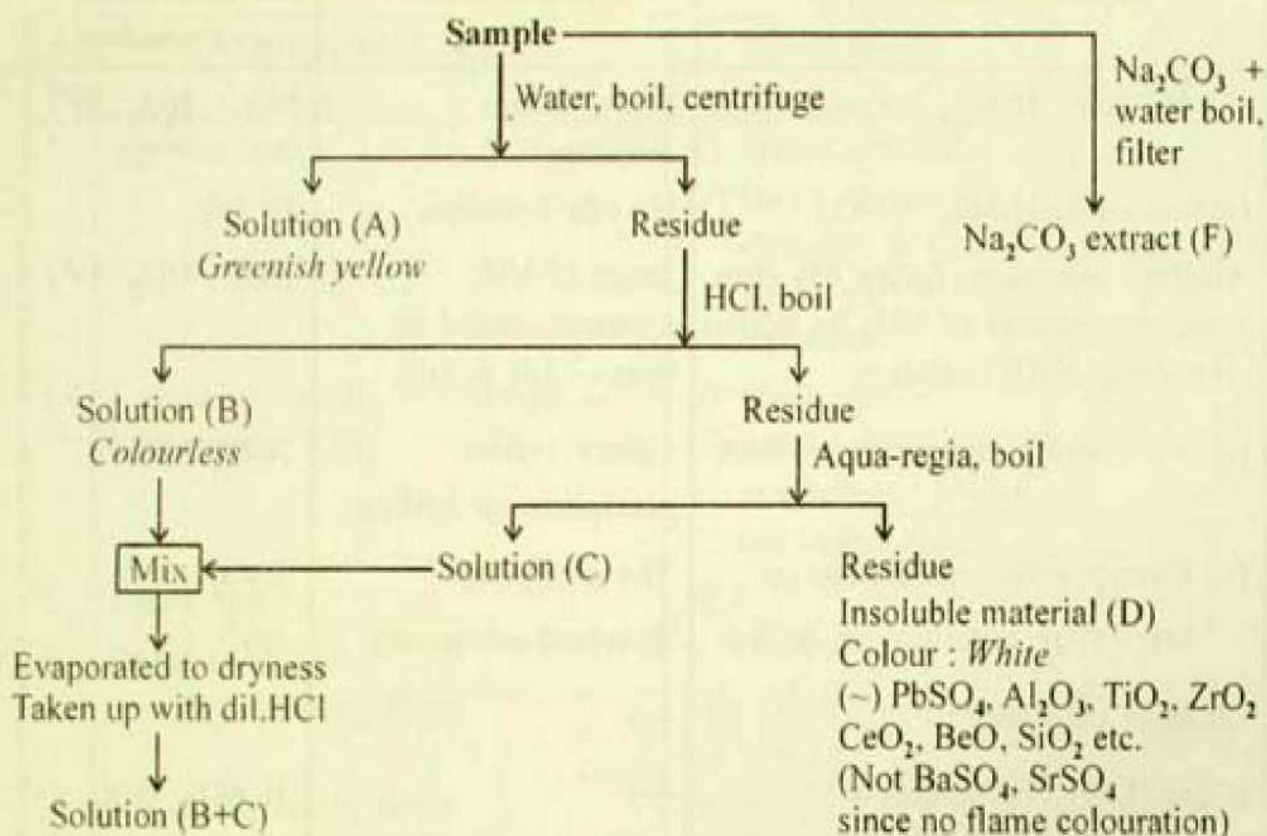
*Rare elements

2. Preliminary dry tests on the solid sample

Sl. No.	Experiments/Reagents	Observations	Inferences/ Probables
1.	Ignition test	(i) White sublimate (ii) Drops of water deposited at the cooler part of the test tube	(~) NH_4^+ , Hg, As, Water of crystallization (✓)
2.	Sample + Na_2CO_3 + Charcoal $\rightarrow$ heated (Fig. 3.27)	(i) Black mirror, (ii) Issuing gas smells NH_3 , turns red litmus blue.	As (✓) NH_4^+ (✓)
3.	Flame test	NCO	INC
4.	Borax-bead test: (i) Oxidizing flame (ii) Reducing flame	Pale yellow when hot and cold. Green when hot, greenish violet when cold.	U (~) U, Ti, Cr, (~)
5.	Microcosmic salt bead test: (i) Oxidizing flame (ii) Reducing flame	Yellow when hot, yellow-green when cold. Greenish yellow when hot, greenish violet when cold.	U (✓) U, Ti, Cr, (~)
6.	Oxidative fusion test on Na_2CO_3 bead.	NCO	Mn, Cr (×)
7.	Action of conc. NaOH solution (Fig 3.27)	Issuing gas (i) smelled NH_3 (ii) turned phenolphthalin paper red. (iii) turned Nessler's reagent paper brown	NH_4^+ (Cf)
8.	Action dil. H_2SO_4 in cold and hot.	NCO	INC
9.	Action of (i) hot conc. H_2SO_4	Brown fumes	NO_3^- , NO_2^- (✓)

Sl. No.	Experiments/Reagents	Observations	Inferences/ Probables
	(ii) hot conc. H_2SO_4 + Cu-turning	Brown fumes deepened	NO_3^- , NO_2^- (✓)
	(iii) hot conc. H_2SO_4 + SiO_2	No oily boubbles	F^- (×)
10.	Alkaline reduction (Zn/NaOH) after complete removal of NH_3 by boiling with conc. NaOH solution	Smell of NH_3 appeared, tested as tests -7 (ii) & (iii).	NO_3^- , NO_2^- (✓)
11.	(i) Ammonium molybdate + HNO_3	Canary yellow precipitate on boiling.	AsO_4^{3-} (~)
	(ii) Canary yellow precipitate of test 11(i)+ tartaric acid, boiled.	The precipitate dissolved completely	AsO_4^{3-} (Cf) PO_4^{3-} (×)
12.	Chromyl chloride test	(-)	Cl^- (×)
13.	(Conc. H_2SO_4 + Methanol)/ Δ : (Tests for borate/ H_3BO_3)	(-)	H_3BO_3 , BO_3^{3-} (×)
14.	Sodium stannite solution.	NCO	INC
15.	Aq- NH_3 solution.	↓ yellow	U (~)
16.	Silicon tetrafluoride- Molybdenum blue-Benzidine blue test for silicate.	(-)	SiO_3^{2-} , SiO_2 (×)
17.	(H_2O_2 + HCl)	NCO	INC
18.	(H_2O_2 + NaOH)	NCO	INC
19.	FeCl_3 solution	NCO	INC
20.	FeSO_4 solution	NCO	INC
21.	$\text{K}_4[\text{Fe}(\text{CN})_6]$ solution	↓ yellow-brown	U (✓)
22.	$\text{K}_3[\text{Fe}(\text{CN})_6]$ solution	NCO	INC
23.	I_2 -azide reaction	(-)	SCN^- , $\text{S}_2\text{O}_3^{2-}$, S^{2-} , oxidants and reductants (×)
24.	Reductive fusion test	(-)	Sulfur containing radicals (×)

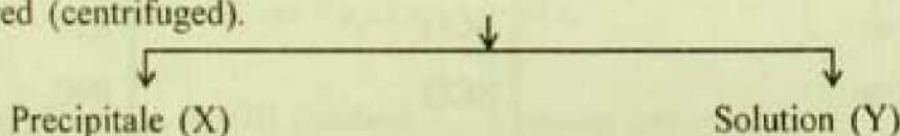
3. Preparation of solutions for wet tests



4. Wet tests for anion radicals in Na_2CO_3 -extract (F)

Note: Since NO_3^- was detected in the preliminary tests, it should be confirmed at this stage by ring test or diazo test after reduction to NO_2^- with the solution F before treatment with $\text{Zn}(\text{NO}_3)_2$. Nitrate would also occur in the aqueous extract (A), since all nitrates except bismuth oxynitrate, are soluble in water.

(a) The Na_2CO_3 extract (F) was neutralized with dil. HNO_3 , CO_2 was boiled off and drops of aq-NH_3 were added until just ammoniacal. Boiled for 2-3 minutes until smell of ammonia disappeared. Drops of concentrated solution of zinc nitrate were added until precipitation was complete, filtered (centrifuged).



The following tests were performed directly on the precipitate (X) and the solution (Y).

(b) Tests for anions on the precipitate (X)

Sl. No.	Experiments/Reagents	Observations	Inferences/ Probables
1.	Acetic acid+Lead acetate	↓ White	INC
2.	Dil. H_2SO_4 + FeSO_4 solution	Blue colouration was not observed	$[\text{Fe}(\text{CN})_6]^{3-}$ (×)

Sl. No.	Experiments/Reagents	Observations	Inferences/ Probables
3.	Dil.HCl + FeCl ₃ solution	Neither red nor blue colouration was observed.	SCN ⁻ , [Fe(CN) ₆ ⁴⁻] (×)
4.	Gutzeit test	(+) Blackening	AsO ₄ ³⁻ , AsO ₃ ³⁻ (✓)
5.	(Precipitate-X + HNO ₃ + Ammonium molybdate)/Δ	No precipitate on just warming. Canary yellow appeared on boiling	PO ₄ ³⁻ (×) AsO ₄ ³⁻ & AsO ₃ ³⁻ (~)
6.	Canary yellow precipitate of test-5 + tartaric acid, boiled	The precipitate dissolved completely	AsO ₄ ³⁻ /AsO ₃ ³⁻ (Cf) but PO ₄ ³⁻ (×)
7.	Precipitate-X + H ₂ S-water + HCl	Milky appearance with yellow precipitate	AsO ₃ ³⁻ , AsO ₄ ³⁻ (~)
8.	Precipitate-X was dissolved in dil.HCl, the solution was treated with magnesia mixture and rendered ammoniacal and then centrifuged.	↓ White crystalline.	AsO ₄ ³⁻ , PO ₄ ³⁻ (~)
9.	Centrifugate of test-8 + H ₂ S-water	(-)	AsO ₃ ³⁻ (×)
10.	(a) Precipitate of test-8, + KI + starch + dil.HCl (b) A few crystals of NaHCO ₃ was added to the blue coloured solution/ spot of test 10(a)	Blue colouration Blue colour was discharged	AsO ₄ ³⁻ (Cf) AsO ₄ ³⁻ (Cf.)
11.	(Quinalizarin + 1:1 H ₂ SO ₄) test for borate/boric acid.	NCO	INC
12.	BaCl ₂ solution + Zr-alizarin-S (red) solution + dil.HCl	No change of colour	F ⁻ (×)
13.	(a) SnCl ₂ solution (b) SnCl ₂ - NH ₄ SCN - HCl	NCO No characteristic colour change	MoO ₄ ²⁻ , WO ₄ ²⁻ (×) MoO ₄ ²⁻ , WO ₄ ²⁻ (×)
14.	Preipitate-X + 1 drop of dil.H ₂ SO ₄ + 3% H ₂ O ₂ solution.	No wine-red colouration.	VO ₃ ⁻ (×)

(c) Tests for anions in the solution (Y).

Sl. No.	Experiments/Reagents	Observations	Inferences/Probables
1.	Solution-Y + HCl + FeCl ₃ solution.	Red colouration was not observed	SCN ⁻ (×)
2.	Solution-Y (colourless) + dil.H ₂ SO ₄ + diphenylcarbazide	No violet colouration	CrO ₄ ²⁻ , Cr ₂ O ₇ ²⁻ (×)
3.	(i) Solution-Y + HNO ₃ + Ba(NO ₃) ₂ solution (ii) Test solution 3(i) + Br ₂ -water	No precipitate	SO ₄ ²⁻ (×)
4.	Solution-Y + 1 drop of fuchsin-bisulfite + Cl ₂ -water.	Blue colouration was not observed.	SO ₃ ²⁻ (×) Br ⁻ (×)
5.	I ₂ - azide test	(-) & NCO	(i) S ²⁻ , SO ₃ ²⁻ , SCN ⁻ (×) (ii) Oxidants (×) (iii) Reductants (×)
6.	Solution -Y + dil.HNO ₃ + AgNO ₃ solution.	No precipitation	(i) Cl ⁻ , Br ⁻ , I ⁻ (×) (ii) BrO ₃ ⁻ & IO ₃ ⁻ (×)
7.	Solution-Y + sulfanilic acid + α-naphthylamine	No red colouration	NO ₂ ⁻ (×)

Note:

Since zinc nitrate was used as a reagent, so, test for NO₃⁻ should be carried out with the original Na₂CO₃ extract (F), or with the aqueous extract (A) or with the original sample itself.

5. Tests with aqueous extract (A)

Sl. No.	Experiments/Reagents	Observations	Inferences/Probables
1.	Colour	Yellowish green	UO ₂ ²⁺ , CrO ₄ ²⁻ Fe ³⁺ (×)
2.	Action of litmus papers	Blue litmus turned red, (acidic reaction)	(×) Fe ³⁺ , UO ₂ ²⁺ , Ti ⁴⁺ ZrO ₂ ²⁺ , and Al ³⁺
3.	Evaporated to dryness and borax bead test performed with the residue. (i) Oxidizing flame	Yellow when hot, pale yellow when cold.	U (×)

Sl. No.	Experiments/Reagents	Observations	Inferences/Probables
3.	(ii)Reducing flame	Green when hot, bottle green when cold.	U (~)
4.	Ring test for nitrate ($\because$ all nitrates are water soluble)	(+)	NO_3^- (Cf)
5.	Diazo coupling test with sulfanilic acid and α -naphthylamine.	(-)	NO_2^- (x)
6.	Diazo coupling test(5) after reduction with Zn-dust.	(+)	NO_3^- (Cf.)
7.	Dil.HCl	No precipitate	Ag^+ , Hg_2^{2+} , Pb^{2+} (x)
8.	Dil HCl + H_2S -water	No precipitate	Gr-II (x)
9.	Ammonium sulfide	$\downarrow$ Brown	Fe^{3+} , Bi^{3+} , UO_2^{2+} (~)
10.	NH_4Cl + aq. NH_3 until alkaline	$\downarrow$ Yellow	UO_2^{2+} , Fe^{3+} , Ce^{4+} (~)
11.	(a) $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution (b) Centrifuged and the brown precipitate of test 11(a) was divided into 2 parts and tested: (i) Dil. HCl solution added (ii) Dil. NaOH solution added	$\downarrow$ Brown The brown precipitate passes into solution The brown precipitate becomes yellow	U, Mo (~) U ($\checkmark$), Mo (x) U (Cf)
12.	(HNO_3 + Ammonium molybdate)/boiled	No precipitate	PO_4^{3-} & AsO_4^{3-} (x)
13.	(a) NH_4Cl + saturated $(\text{NH}_4)_2\text{CO}_3$ solution + NH_3 . (b) Centrifugd and an excess of saturated $(\text{NH}_4)_2\text{CO}_3$ solution was added to the precipitate and warmed gently.	$\downarrow$ White The precipitate dissolved completely producing a yellow solution	Gr-IV, U (~) U (Cf) Gr-IV (x)
14.	Na_2HPO_4 solution	$\downarrow$ White (i) soluble in dil.HCl, (ii) insoluble in dil.acetic acid. (iii)turned yellow when stirred with NaOH solution.	UO_2^{2+} , Mg^{2+} (~) UO_2^{2+} (Cf) Mg^{2+} (x)

Therefore, the aqueous extract (A) contained : UO_2^{2+} and NO_3^- ions.

6. Tests with HCl extract (B + C)

Sl. No.	Experiments/Reagents	Observations	Inferences/ Probables
1.	Diluted with water, warmed and H_2S -water added.	↓ Yellow, with milky white appearance	Cd, As, Sb, Sn (~) & also oxidants to H_2S (~)
2.	The yellow precipitate obtained in test (1) was centrifuged and treated with $(NH_4)_2S_x$ solution.	The precipitate dissolved completely, but reappeared on acidification with HCl	As, Sb, Sn (✓)
3.	(i) The yellow precipitate obtained in test (2) was boiled with conc.HCl. (ii) Centrifuged, and the centrifugate was tested for Sn and Sb individually. (iii) The yellow precipitate was treated with 2M NH_3 and 3% H_2O_2 , warmed gently and treated with magnesia mixture and the solution rendered ammoniacal.	The precipitate remained undissolved (-) ↓ White crystallise	As (✓) Sn and Sb (×) As (Cf)
4.	Original HCl extract (B+C) + ammonium molybdate+ HNO_3 , boiled gently.	↓ Canary yellow, soluble on boiling with tartaric acid	AsO_4^{3-} (Cf)
5.	Centrifugate from test (1) was acidified with a few drops of conc. HNO_3 , boiled with a small amount of filter paper pulp to coagulate the colloidal sulfur and centrifuged. The clear centrifugate was evaporated to dryness.	A residue was left	Group (III-V) (✓)
6.	The residue of test-5 was taken up with water and the following tests were performed with this extract: (i) (Extract + NH_4Cl + NH_3 until ammoniacal) warmed. (ii) Test solution 6(i) + H_2S -water (iii) (Extract + NH_4Cl + $(NH_4)_2CO_3$ + NH_3) until ammoniacal	No precipitate No precipitate No precipitate	Gr-III A (×) Gr-III B (×) Gr-IV (×)

Sl. No.	Experiments/Reagents	Observations	Inferences/ Probables
	(iv) (Extract + $\text{Na}_2\text{HPO}_4 + \text{NH}_3$) until ammoniacal	↓ White crystalline	Mg^{2+} (✓)
	(v) Extract + sodium cobaltinitrite	↓ Yellow	$\text{K}^+, \text{NH}_4^+$ (✓)
	(vi) Extract + Zincuranyl acetate	No precipitate	Na^+ (×)
	(vii) Titan yellow test	(+)	Mg^{2+} (Cf.)
	(viii) Quinalizarin test.	(+)	Mg^{2+} (Cf.)
7.	(Original HCl extract (B+C) + conc. NaOH) was warmed (Fig. 3.29) gently and the issuing gas was tested as follows:		
	(i) Smell	(i) Smells NH_3	NH_4^+ + (Cf)
	(ii) Red litmus paper	(ii) Turned blue	NH_4^+ (✓)
	(iii) Phenolphthalin paper	(iii) Turned red, red colour disappeared on drying	NH_4^+ (Cf)
	(iv) Nessler's reagent paper	Brown spot	NH_4^+ (Cf)
8.	Original HCl extract (B+C) + conc. NaOH, boiled to remove NH_3 completely. Cooled, acidified with acetic acid and sodium cobaltinitrite was added.	No precipitate	K^+ (×)

Therefore, the HCl extract (B+C) contained: NH_4^+ , AsO_4^{3-} and Mg^{2+} ions.

7. Identification of the insoluble residue (D)

Sl. No.	Experiments/Reagents	Observations	Inferences/ Probables
1.	Examination of colour	White	Al_2O_3 , TiO_2 , ZrO_2 , BeO , CeO_2 , SiO_2 , sulfates of Ba, Sr, Pb.
2.	Flame test (cf. Sect. 6.5)	No characteristic flame colour	BaSO_4 , SrSO_4 (×)
3.	Ammonium acetate extract + K_2CrO_4	No yellow precipitate	PbSO_4 (×)
4.	NaOH-extract, neutralized with acetic acid and subjected to alizarion-S test	(-)	Al_2O_3 (×)
5.	(a) Silicon tetrafluoride test, combined with molybdenum blue-benzidine blue test for silicate, silica.	(-)	SiO_2 & silicates (×)

Sl. No.	Experiments/Reagents	Observations	Inferences/ Probables
	(b) Na_2CO_3 bead test combined with molybdenum blue benzidine blue test.	(-)	SiO_2 & SiO_3^{2-} (x)
6.	Borax bead test: Oxidizing flame Reducing flame	Yellow when hot, colourless when cold. Grey when hot, pale violet when cold.	TiO_2 (~) TiO_2 (~)
7.	Microcosmic salt bead test: Oxidizing flame Reducing flame	Colourless when hot and cold Yellow when hot violet when cold	TiO_2 (~) TiO_2 (~)
8.	KHSO_4 - fusion extract was subjected to the following tests: (a) Extract + H_2O_2 (i) A few crystals of NH_4HF_2 was added to the yellow solution-8(a) . (ii) A pinch of H_3BO_3 was added to the mixture 8(a)(i) and boiled (b) Extract + H_2O_2 + aq - NH_3 warmed (c) 4-Dimthylaminoazophenyl arsonic acid test. (d) Alizarin-S test (e) Extract + ammoniacal AgNO_3 (f) Extract + NaOH + benzidine	Yellow colouration appeared Yellow colour discharged Yellow colour reappeared NCO (-) (-) No blackening No blue colouration	Ti^{IV} (Cf) Ti^{IV} (Cf) Ti^{IV} (Cf) INC ZrO_2 (x) Al_2O_3 (x) Ce^{III} (x) CeO_2 (x)
9.	$(\text{Na}_2\text{CO}_3 + \text{K}_2\text{CO}_3)$ fusion extract was acidified with HNO_3 and was treated with $\text{Ba}(\text{NO}_3)_2$ solution.	No precipitate	SO_4^{2-} (x)
10.	The residue of $(\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3)$ fusion extract was subjected to flame test	No characteristic flame colouration other than golden yellow of Na	Ba & Sr (x)

Therefore, the insoluble residue D was TiO_2 .

8. Probable composition

Radical detected

- (i) Aqueous extract : UO_2^{2+} and NO_3^-
- (ii) HCl extract : NH_4^+ , Mg^{2+} , AsO_4^{3-}
- (iii) Insoluble material : Ti^{IV} (TiO_2)

Since only UO_2^{2+} and NO_3^- ions were present in the aqueous extract, so, $\text{UO}_2(\text{NO}_3)_2$ was present. As the HCl extract contained NH_4^+ , Mg^{2+} and AsO_4^{3-} ions, these might occur as $\text{NH}_4\text{MgAsO}_4$, since this could be the only possible water insoluble but HCl-soluble compound, that might have formed out of these three radicals. The insoluble part was unambiguously TiO_2 . AsO_4^{3-} in the HCl extract (B+C) oxidized H_2S , precipitating colloidal sulfur and As_2S_3 .

Yellowish green colour and weakly acidic nature of the aqueous extract further supported the presence of UO_2^{2+} ion. Deposition of water on the cooler part of the test tube in the ignition test indicated the presence of water of crystallization in one, or more constituents of the sample. Uranyl nitrate $\text{UO}_2(\text{NO}_3)_2$ is known as its hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ammonium magnesium arsenate, $\text{NH}_4\text{MgAsO}_4$ is also likely to exist as hexahydrate, $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$, like its phosphate analogue. White colour of the insoluble residue and the presence of Ti^{IV} in it, suggested TiO_2 . Therefore, the most probable composition of the mixture should be : $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{NH}_4\text{MgAsO}_4 \cdot 6\text{H}_2\text{O}$, TiO_2 .

9. Tests to be described

- (i) NH_4^+ ... Preliminary tests (2)7 using phenolphthalin paper, Nessler's reagent paper and confirmation by cobaltinitrite test, tannic acid- AgNO_3 test.
- (ii) NO_3^- ... Preliminary tests (2)9, confirmation by ring test and diazo test after reduction to nitrite.
- (iii) AsO_4^{3-} ... Ammonium molybdate - tartaric acid test, magnesia mixture test, Gr-IIB analysis, separation from phosphate and arsenite, oxidation of iodide-starch paper.
- (iv) Mg^{2+} ... Gr-V analysis after separation of other metals using POS- NH_3 reagent, confirmation by titan yellow test, quinalizarin test, hypiodite test.
- (v) UO_2^{2+} ... Borax bead test, microcosmic salt bead test, confirmation by $\text{K}_4[\text{Fe}(\text{CN})_6]$ test followed by treatment with NaOH and $(\text{NH}_4)_2\text{CO}_3$ solutions.
- (vi) TiO ... H_2O_2 - NH_4HF_2 - H_3BO_3 tests with KHSO_4 fusion extract.

CHAPTER - 10

Applications of Spot Reactions: Detection of Trace Quantities of some Elements and Radicals in Real Samples

10.1 Introduction

Spot reactions described in the previous chapters may often be applied with, or, without modification for rapid and indisputable detection of some specific elements or compounds or radicals in real samples, eg, minerals and ores, metals and alloys, water and other liquid samples, natural products, scientific, technical, industrial and domestic materials. Some tests may be directly applied on the solid, or, liquid sample itself. When the amount of the element to be tested is too small in the sample, that direct testing by spot reactions is not possible, the trace element, or the radical may be accumulated on some chemically, or, structurally analogous solid materials serving as *collectors* or *trace catchers*, which act through coprecipitation, adsorption, or formation of mixed crystals. The collector to be selected, should not interfere in the actual test of the radical of interest. Otherwise, the collector should be separated from the test solution, or, should be masked by complex formation before applying the sensitive spot reaction. Following are the few examples of innumerable number of applications of spot reactions in testing purity of technical and useful materials and detecting trace elements in minerals.

10.2 Detection of traces of copper in water, food stuff and pharmaceuticals

Copper is an essential trace element in the biological system. It is an integral part of the active sites of several metallo-proteins and redox metallo-enzymes. Amounts less than 0.001% are harmless, but at higher concentration it is toxic. It is, therefore, often necessary to perform tests for copper while examining food stuff, pharmaceuticals and other useful materials, even distilled water. Tests applied for detecting trace quantities of copper involve two steps : (i) concentration of the test sample and (ii) the actual chemical test. The first steps are essential for bringing the concentration of copper within the *limit of identification* of the test, whereas, the second steps are based on the same principles as described in chapter-4 (cf. Sect 4.6).

(i) Detection of copper in water samples

Take ~50-100 ml of the water sample in a conical flask, add ~0.1g of calcium fluoride, or, talc and shake for about 10 minutes. By this operation, traces of copper that may be present in water, collects through adsorption on the solid and the supernatant liquid (i.e, water) becomes

absolutely free from copper. Filter, or, centrifuge in parts and discard the liquid. Traces of copper collected on the solid is sufficient for catalytic effect on the reaction:



as described in Sect. 4.6

Place a small amount of the collector slurry on a cavity of a spot plate. In an adjacent cavity, place the same amount of the same collector slurry prepared by shaking the same amount of copper-free water with same amount of the adsorbent. Now add 1 drop of ferric thiocyanate solution and 2 drops of 0.1N sodium thiosulfate solution to both the cavities and stir with two separate glass rods. Red colour of ferric thiocyanate complex tends to disappear. A comparatively faster rate of disappearance of the red colour by the collector slurry of the sample water compared to that of the copper-free water collector slurry indicates the presence of copper in the sample water.

(ii) Detection of copper in food stuff and pharmaceuticals

In detecting copper in food stuff, drugs and pharmaceuticals the sample has to be first treated with a strong oxidizing agent, viz. concentrated nitric acid, to decompose the organic matters completely. The excess oxidant should also be decomposed by evaporating the reaction mixture to dryness. Dilute HCl, or, HNO_3 extract of the residue should be subjected to chemical tests.

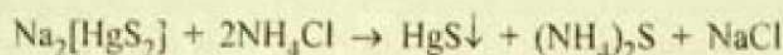
Place 0.2 to 1.0 g of the substance in a small porcelain or, silica crucible, heat first gently, then strongly inside a **FUME CUPBOARD** to ash the materials. Cool and moisten the residue with 1-2 drops of conc. HNO_3 and heat strongly as before until the black particles (if any) due to carbon disappear. Cool and add a few drops of conc. HCl and heat gently to remove the nitrous fumes. Add ~ 2 ml of distilled water and boil gently for 1-2 minutes to dissolve the soluble components in the residue. Filter the solution with a cotton filter (Fig. 3.19b), or, with an Emich filter stick (Fig. 3.21). Add a few crystals of ammonium fluoride or ammonium bifluoride to mask iron (III) if any, as $[\text{FeF}_6]^{3-}$ complex ion. Add 1 drop of 0.25 M zinc sulfate, or, (1%) Zn-acetate solution followed by 1-2 drops of ammonium mercuriothiocyanate reagent. Shake well. A violet precipitate due to the formation of mixed crystals of $\text{Cu}[\text{Hg}(\text{SCN})_4]$ and $\text{Zn}[\text{Hg}(\text{SCN})_4]$ indicates the presence of copper in the sample (cf. Sect. 4.6).

10.3 Detection of traces of lead in water, sulfuric acid and alkali sulfates, enamels, tin platings and in criminalistic investigations

Lead is a heavy metal and is toxic to the living organisms. Because of its softness, Pb^{2+} ion binds to the thiol ($-\text{SH}$) groups of the proteins and thereby denatures the enzymes and disrupts the biosyntheses of important biomolecules. Lead enters the biological systems mainly through contaminated water. Auto exhaust contains considerable amounts of lead compounds because of the use of certain alkyl and haloalkyl lead derivatives as *antiknock compounds* in gasoline. Small amounts of lead that accumulate in human organisms are eliminated at very slow rate. Therefore, testing of water samples and other useful materials for traces of lead content is very important from medical and public health stand points.

Sodium rhodizonate test (Sect. 4.4) is one of the most sensitive tests for lead with a *limit*

of identification of 0.1% of Pb and a dilution limit of 1 : 5×10^5 . Sensitivity of the test may be greatly increased by concentrating lead by coprecipitating lead sulfide, PbS, ($K_{sp} = 2.5 \times 10^{-27}$) upon more insoluble mercuric sulfide HgS, ($K_{sp} = 1.6 \times 10^{-52}$) by treating the test solution (eg. water sample, solution of alkali metal sulfates or, other alkali metal salts and even sulfuric acid) with sodium mercurisulfide, $\text{Na}_2[\text{HgS}_2]$, solution in presence of ammonium chloride:



Mercuric sulfide that precipitates, acts as a *catcher* for trace amounts of lead sulfide which may remain dissolved in the solution because of its comparatively higher solubility than mercuric sulfide. If this black mixture of lead and mercury sulfides is treated with H_2O_2 , dried and then ignited, mercury sulfide volatilizes out, whereas, black coloured lead sulfide is oxidized to white coloured insoluble lead sulfate:



If the residue of PbSO_4 , after washing with a little very pure distilled water, is subjected to rhodizonate test, *dilution limit* of $\sim 1 : 10^7$ to $1 : 10^8$ may be achieved in a volume of 100 ml, which correspond to $\sim 1 \times 10^{-6} \%$ to $10^{-8} \%$ of Pb.

Reagents

(i) $\text{Na}_2[\text{HgS}_2]$ solution

Dissolve 13.6g of HgCl_2 in ~ 60 ml of hot water. Treat the solution with solid Na_2S , when HgS is precipitated. Add little more solid Na_2S and then a concentrated solution of Na_2S until the precipitate of HgS passes into solution as $[\text{HgS}_2^{2-}]$ complex ion. Dilute to 100 ml with water and filter if necessary.

(ii) Buffer solution of pH ~ 2.8

Dissolve 1.5g of tartaric acid and 1.9 g of sodium hydrogentartrate in water and dilute the solution to ~ 100 ml.

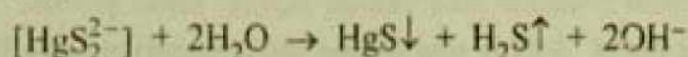
(iii) Sodium rhodizonate solution

Dissolve ~ 2 mg of the salt in ~ 10 ml of water. Use of freshly prepared solution is recommended, as the reagent does not keep for more than two days even if it is preserved in a refrigerator.

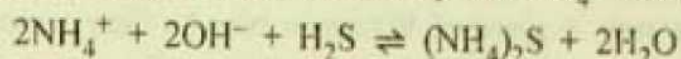
Procedure

(i) Traces of lead in water, sulfuric acid and alkali sulfate

Place ~ 10 ml of the sample solution to be tested (viz, water, solution of alkali metal sulfate, dilute sulfuric acid etc.) in a porcelain crucible (~ 30 ml), add drops of the $\text{Na}_2[\text{HgS}_2]$ reagent solution ($\sim 0.3 - 0.5$ ml) and stir with a glass rod. HgS is partially precipitated owing to hydrolysis of $[\text{HgS}_2^{2-}]$ ion,



Add ~1g of very pure (GR) NH_4Cl and digest the mixture briefly, when HgS is completely precipitated as the OH^- ions are neutralized by the NH_4^+ ions,



As the black precipitate of HgS settles down at the bottom of the crucible, remove the supernatant liquid with the aid of a capillary dropper. Wash the precipitate with very pure water by stirring with a glass rod and remove the supernatant liquid as before. Now add ~5ml of 3% H_2O_2 and stir with a glass rod for 3-4 minutes and then remove the supernatant liquid as before. Now place the crucible with its contents on a hot plate inside a **FUME CUPBOARD**, when the black precipitate of HgS volatilizes off and the black precipitate of PbS is transformed to white coloured sparingly soluble PbSO_4 . Heat the crucible gently for ~1 minute, cool to room temperature and moisten the residual mass, if any, with 5 drops of the rhodizonate reagent. Stir with a glass rod, suck off the supernatant liquid with the aid of a capillary tube. Add 2-3 drops of the buffer solution ($\text{pH} \sim 2.8$) and 3-4 drops of very pure water. Yellow colour of the excess reagent is bleached and the red particles of lead rhodizonate are clearly visible against the white bottom of the crucible if the sample solution contains lead. Run a blank test using the same volume of very pure water in place of the sample water.

To have an idea about the relative amount of lead present in the sample water solution, the test may be carried out with same volume of the standard solutions containing known amounts of lead and the colour of the lead rhodizonates formed from the sample water may be compared with the corresponding colours formed with the standard solutions.

(iii) Detection of lead in enamels and tin platings

Lead in enamels

Clean the surface of the enamel to be tested and spot the surface with a drop of concentrated nitric acid and slowly evaporate the acid to dryness by gentle heating inside a **FUME CUPBOARD**. If lead is present, it is converted to lead nitrate. Moisten the spot with a drop of 10% potassium iodide solution. A yellow spot (or needles) of lead iodide (PbI_2) appears if lead is present.

Lead in tin platings

Wash the tinned surface, free from grease and dust materials accordingly and finally wash with alcohol and ether. Place a drop of concentrated nitric acid, or, acetic acid on the surface and warm gently inside a **FUME CUPBOARD** until the acid is evaporated. A grey fleck is formed on the surface where acid was added, due to the formation of metastannic acid and lead nitrate (or acetate), if lead is present. Add a drop of 5% potassium iodide solution on the spot. Yellow needles of lead iodide appear if lead (down to 1%) is present.

(iii) Lead in criminalistic investigations

When uncoated lead bullets, discharged from fire arms, strike on living or, non-living

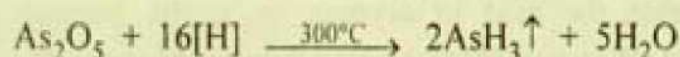
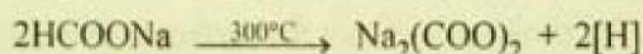
objects, the impact area or, the wound adheres traces of lead, detection of which is often necessary for crime investigation. Presence or, absence of Pb^{2+} may be ascertained by subjecting the impact area to rhodizonate test. A piece of Whatman No. 1 filter paper moistened with tartaric acid tartarate buffer solution ($pH \sim 2.8$) is pressed over the spot for several minutes and a drop of rhodizonate reagent is added. Red flecks are formed if Pb^{2+} is present. The position of the spot also indicates the location of lead in the substrate.

10.4 Detection of traces of arsenic in minerals

Arsenic is moderately toxic to plants and highly toxic to mammals. Serious arsenic pollution problem arises from mining, burning of coal, use of insecticides, herbicides and impure sulfuric acid. Arsenic (III) i.e., arsenite (AsO_3^{3-}) may bind to the thiol ($-SH$) groups in proteins and denatures the enzyme proteins. Arsenic (V), i.e., arsenate (AsO_4^{3-}), because of its chemical similarity to phosphate (PO_4^{3-}), which is one of the major essential chemical entity in the biological system, may replace phosphate and thereby may uncouple *phosphorylation* from *metabolic oxidation*. Arsenic poisoning may lead to loss of hair, gastrointestinal problems, dermatitis and skin cancer. Therefore, special procedure or, technique should be adopted in handling arsenic bearing materials.

The principle of detection of trace quantities of arsenic in minerals, pesticides and other materials involves the transformation of arsenic bearing compounds into arsine (AsH_3) gas followed by its reaction with (i) silver nitrate or, (ii) mercuric bromide, impregnated on a drop reaction paper, where a black spot, or, a yellow stain respectively is formed.

Arsenic in the forms of arsenic oxide, arsenate or arsenite, when heated at $300^\circ C$ with sodium formate (m.p. $250^\circ C$) or sodium borohydride, is transformed to arsine gas due to reduction of these oxygen bearing arsenic compounds:



Sulfide interferes in the test, as H_2S produced from the reaction of sulfide with sodium formate or sodium borohydride, produces black spot due to Ag_2S . Interference due to sulfide may be eliminated by igniting the powdered material in a micro crucible (in a **FUME CUPBOARD**), when sulfide is oxidized to sulfate.

Procedure

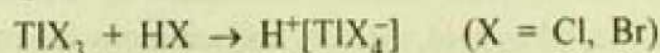
Take ~ 1 mg of the pulverized material in a micro crucible and ignite the same inside a **FUME CUPBOARD**. Mix the ignited material with 10-15 times its bulk of sodium formate, previously dried at $120^\circ C$. Transfer the mixture into a semi-micro test tube, plug the mouth of the test tube with a piece of clean cotton wool, place a filter paper, impregnated with a drop of 10% $AgNO_3$ or mercuric bromide solution at the mouth of the test tube (Fig 3.27

a) and heat the test tube inside a **FUME CUPBOARD**. A black fleck is formed on the AgNO_3 paper, or yellow-brown stain on HgBr_2 paper, if arsenic is present in the material. (cf. Sect. 4.8).

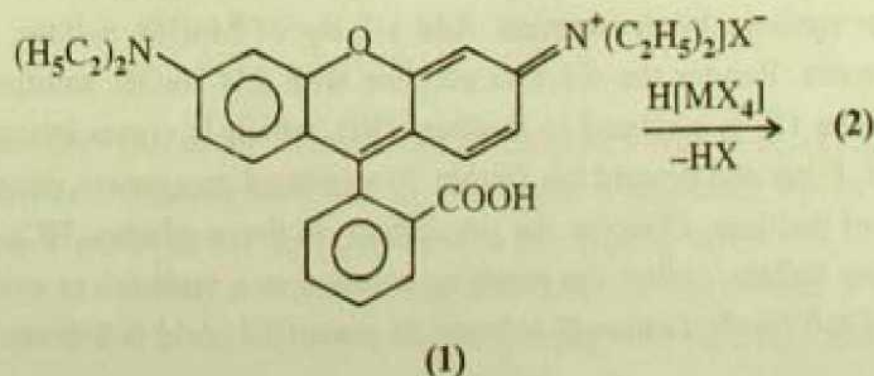
10.5 Detection of traces of thallium in mineral water samples and in forensic, medical and criminalistic investigations.

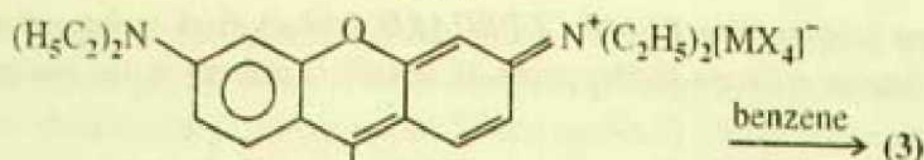
Thallium is a trace element in the earth's crust (0.00045g. Kg^{-1}) and in ocean water ($1 \times 10^{-6} \text{ mg.lit}^{-1}$). It exists in two oxidation states, Tl^+ and Tl^{3+} . The radius of Tl^+ ion is slightly larger than that of K^+ ion (eg, for coordination number 6, 8 and 12, radii of K^+ ion are 152, 165 and 178 pm and those of Tl^+ ion are 164, 173 and 184 pm respectively). Because of such comparable size, Tl^+ ion may compete with K^+ ion in the process of its transport across biological membrane. More over, due to higher polarizability of Tl^+ over K^+ ion, the former binds more strongly to the membrane proteins and enzymes requiring K^+ ion for their activity. As a matter of fact, thallium, particularly Tl^+ , is a deadly poisonous and toxic element to the biological system. Thallium contamination may lead to hair loss, gastroenterities, bone damage, kidney failure, finally death. It is, therefore, very important to test for thallium in technical materials, minerals, and natural water samples. Thallium test is often carried out in forensic, medical and criminalistic investigations.

Trace quantities of thallium in the form of Tl^{III} chloride, or, bromide maybe detected from the yellow fluorescence of Tl^{III} - halide-rhodamine B complex in benzene solution. Acid solution of rhodamine-B, containing the cation (1) of the dye stuff, reacts with TlCl_3 or TlBr_3 in presence of HCl or HBr to produce violet precipitate of sparingly soluble dye stuff salts (2) of the halocomplex ions $[\text{TlCl}_4^-]$ or $[\text{TlBr}_4^-]$ derived from the reactions Tl^{III} halides with the corresponding halogen acids,

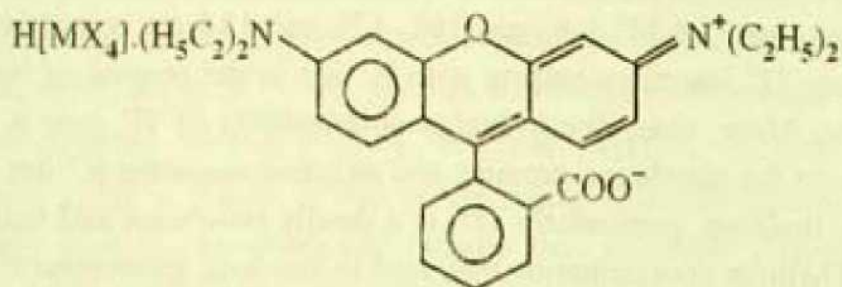


On shaking with benzene (or ether), the product is extracted into the organic layer in its zwitterionic form (3), producing a red colour in the organic layer, which displays an intense orange-yellow fluorescence on exposure to ultraviolet light. Neither the solution of the dye stuff in HCl , or, HBr on shaking with benzene or ether nor the solid water-insoluble Tl^{III} -halide-rhodamine B salts (2) themselves without shakling with benzene, produce any fluorescence.





(2)



$\text{M} = \text{Tl, Au, Hg; X} = \text{Cl, Br}$

(3)

If the thallium content of the sample solution is too low, then the precipitate of (2) may not be visible, nor there may be any change of colour of the reagent, but the fluorescence in the benzene layer may be revealable. Gold and mercury interferes by producing similar fluorescence in the benzene layer.

Antimony (V) - rhodamine-B compound dissolves in benzene, producing a red colouration (*cf.* Seet 4.9). Interference due to these metals may be eliminated by treating the acidic test solution with a copper or a brass wire, when gold, mercury and antimony are reduced to metallic state and are deposited on the Cu wire as a coating. Tl^{III} is reduced to Tl^{I} , which is not reduced by the copper, or, brass wire to the elemental state. For detection of ultra trace quantity of thallium, freshly precipitated hydrous manganese dioxide, $\text{MnO}(\text{OH})_2$, may be used as a collector.

Detection of thallium in mineral water

Take ~ 500 ml of sample water, acidify with a few drops of HCl, add some bright copper turnings and shake vigorously to reduce gold, mercury and antimony to their elemental states. Remove the copper turnings by decantation. Add 1-2 mg of Mn(II)- sulfate, or, chloride and an excess of Br_2 -water. Render the solution alkaline with 2M NaOH solution and stir with a glass rod. Thallium (I), is oxidized to thallium (III), which is coprecipitated with hydrous manganese dioxide. Filter and discard the filtrate. Precipitated manganese dioxide will contain the entire amount of thallium. Dissolve the precipitate in drops of conc.HCl containing some sodium or potassium sulfate, collect the resulting solution in a semi-micro centrifuge tube and treat with drops of 0.05% rhodamine-B solution in conc.HCl. Add 6-8 drops of benzene and

then shake vigorously. Allow the layers to separate (centrifuge if necessary). The benzene layer appears red-violet to pink and displays a yellow fluorescence on exposure to *uv*-light. Compare with a blank test, using distilled water, as benzene often shows blue fluorescence.

Limit of identification: 0.03 γ of Ti

Limit of dilution: 1 : 1 $\times 10^9$

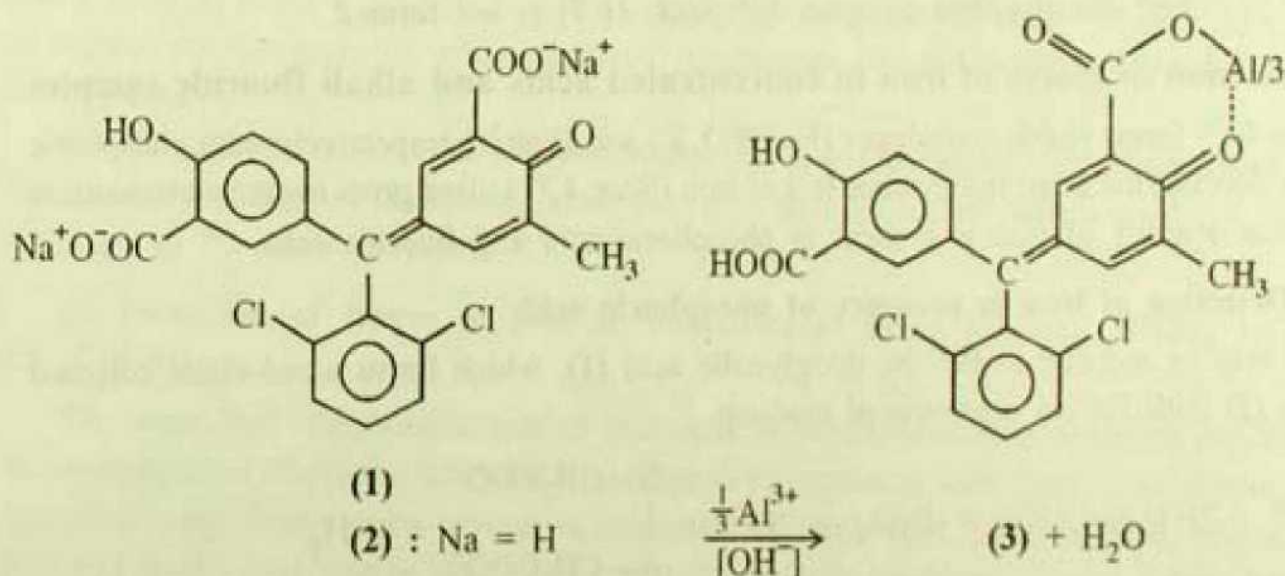
10.6 Detection of traces of aluminium in water samples

Although aluminium may activate certain enzymes, viz. succinate dehydrogenase, but it is moderately toxic to most plants and slightly toxic to mammals. The metal is, however, relatively inaccessible except in acidic medium due to insolubility of $\text{Al}(\text{OH})_3$ in neutral medium.

Localized accumulation of aluminium in the brain cells is the cause of *Alzheimer's disease*, which is the most prevalent form of senile dementia.

As alum is extensively used in water treatment, presence of traces of aluminium in treated water is not unlikely. It is, therefore, important to test the domestic water samples for aluminium content.

The most specific reagent for rapid detection of traces of aluminium in water samples is the oxytriphenylmethane dye, Chrome Fast Pure Blue (I). The reagent reacts with weakly acidic solution containing traces of aluminium to give a yellow precipitate of slightly water soluble dye acid (2). On rendering the mixture alkaline with ammonia followed by acidification with $\text{dil. H}_2\text{SO}_4$ and shaking with ether, the ethereal layer assumes a yellow colour due to dissolution of the dye acid (2) and the red coloured aqueous layer contains the inner complex of aluminium with the dye stuff, in which aluminium remains as a constituent of the anion (3)



The complex (3) is so stable that it is not decomposed even in (1:1) H_2SO_4 medium. $\text{Cr}(\text{III})$ interferes in this test. Interference due to zirconium is eliminated by its complex formation with sulfate ion if acidification is carried out with H_2SO_4 instead of HCl . For precipitation of $\text{Al}(\text{OH})_3$ from a solution containing trace quantities of aluminium, a small amount FeCl_3 solution has to be added to coprecipitate $\text{Al}(\text{OH})_3$ along with $\text{Fe}(\text{OH})_3$. Sensitivity of the colour

reaction may be further increased by treating the solution with a slight excess of MgCO_3 before addition of the reagent.

Procedure

To 25-50 ml of the water sample, add one drop of 1% solution of ferric chloride (or sulfate) and drops of aqueous ammonia ($\sim 1M$), (or a few mg. of magnesium carbonate powder) avoiding large excess. Hydrous ferric oxide precipitates and serves as a collector for the more soluble hydrous alumina (pK_{sp} : $\text{Fe}(\text{OH})_3$, 37.2 – 38.2; $\text{Al}(\text{OH})_3$, 32.3). Centrifuge the suspension in portions and dissolve the combined precipitates in a drop or two of a mixture of $2N \text{H}_2\text{SO}_4$, add a few grains of very pure (Al-free) zinc dust to reduce Fe^{3+} to Fe^{2+} which does not react with the dye. Filter off the excess zinc using a cotton filter (Fig. 3.19b). To the resulting solution, add one drop of 5% aqueous solution of Chrome Fast Pure Blue reagent and then acidify with a drop of 1:1 H_2SO_4 . Add 10-15 drops of diethyl ether and shake. Any excess dye enters into the ether layer and the lower aqueous layer becomes magenta, or pink coloured according to the aluminium content.

Limit of identification: 0.4γ of Al in 20 ml of water.

Limit of dilution: $1 : 5 \times 10^7$

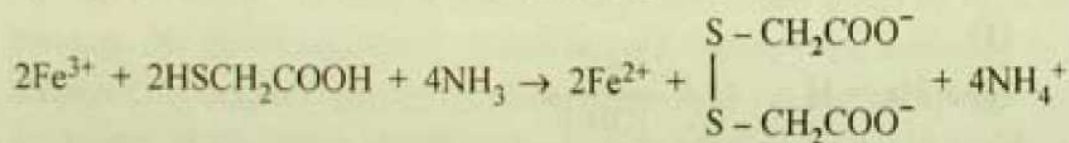
- Note:** (i) The method is not suitable for detection of aluminium in sea water, where the metal does not remain in the form of a simple inorganic ion, but remains in the colloidal form.
- (ii) In stead of zinc dust, thioglycolic acid may also be used for reduction of Fe^{3+} to Fe^{2+} . In strongly acidic medium used for this test of Al^{3+} , the red-violet Fe^{2+} -thioglycolate complex (*cf.* Sect. 10.7) is not formed.

10.7 Detection of traces of iron in concentrated acids and alkali fluoride samples

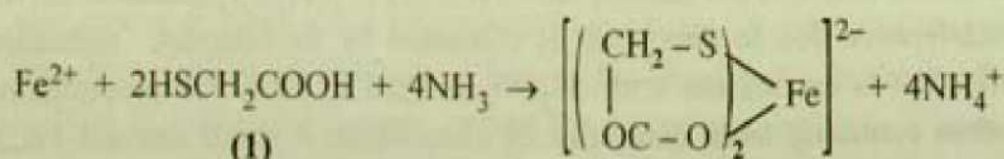
Since Fe^{III} forms stable complexes $[\text{Fe}(\text{HPO}_4)_2^-]$ and $[\text{FeF}_6]^{3-}$ respectively with phosphoric acid and fluoride, the usual thiocyanate test of iron (Sect. 4.11) often gives negative observation when trace quantity of iron is present in phosphoric acid and fluoride salts.

(a) Detection of iron in presence of phosphoric acid

Fe^{III} may be reduced to Fe^{II} by thioglycolic acid (1), which forms a red-violet coloured complex (2) with Fe^{II} in ammoniacal medium.



(1)



(1)

(2)

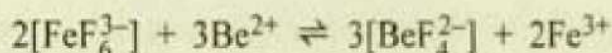
This colour reaction is even more sensitive than the Fe^{III} -thiocyanate reaction. The sensitivity of this test may be further improved by using thioglycolic acid containing some 1,10-phenanthroline or 2,2'-bipyridine.

Procedure

Take one drop of the test sample (phosphoric acid) in a semi-micro test tube, dilute with 2-3 drops of water, add one drop of concentrated (80%) thioglycolic acid and one drop of 1,10-phenanthroline (or, 2,2'-bipyridine). Add drops of (1:1) aq- NH_3 solution until faintly ammoniacal. Warm gently on a hot water bath. A red-violet to blue-violet colour appears if iron is present.

(b) Detection of iron in alkali fluoride

(i) Fe^{III} remains masked as $[\text{FeF}_6]^{3-}$ complex ion in presence of fluoride. Fe^{III} maybe demasked from this complex by treating the solution with a beryllium salt solution. Small Be^{2+} ion forms slightly more stable complex with F^- ion than does the larger Fe^{3+} ion, so that the displacement equilibrium,



remains shifted to the right hand side. If thiocyanate is present in this condition, a red colour is developed due to the formation of $[\text{Fe}^{\text{III}}(\text{SCN})_2]^{+}$ complex.

Procedure

Place a drop of the test solution on a spot plate, add a few crystals of NH_4SCN (or KSCN) and a drop of dilute ($\sim 2M$) HCl . Add 1-2 drops of beryllium chloride (or beryllium nitrate or sulfate) solution and stir with a glass rod. Appearance of a red to pink colouration indicates the presence of iron.

(ii) Thioglycolic acid - 1, 10-phenanthroline (or, 2, 2'-bipyridine) reagent described before for detection of iron in phosphoric acid, may also be applied for detection of iron in alkali fluorides by the same procedure.

(c) Detection of traces of iron in concentrated acids (H_2SO_4 , HNO_3 , HCl and CH_3COOH)

The usual Fe^{III} -thiocyanate test of iron fails in concentrated acid solutions due to rapid decomposition of thiocyanic acid and its oxidation by oxidizing acids such as nitric acid. Trace amount of iron that may be present in concentrated nitric acid, sulfuric acid, hydrochloric acid and acetic acid, maybe precipitated as hydrous ferric oxide on alumina, which functions as a collector, or, trace catcher and the mixed precipitate maybe subjected to thioglycolic acid-1,10-phenanthroline (or 2,2'-bipyridine) test.

Procedure

Place 1 drop of 2% solution of aluminium sulfate and 1 ml of the test sample (conc. HNO_3 , H_2SO_4 , HCl or, acetic acid) in a semi-micro centrifuge tube (~ 5 ml). Make the solution alkaline by carefully adding drops of concentrated ammonia, while cooling the mixture. Centrifuge the

mixture, and discard the centrifugate. The precipitate remains gathered at the constricted part of the centrifuge tube. Treat the precipitate with 1-2 drops of 2% solution of 1,10-phenanthroline (or, 2,2'-bipyridine) in 80% thioglycolic acid and warm the mixture gently by placing on a hot water bath (Fig. 3.15). Depending upon the quantity of iron present, a pink to red colour appears.

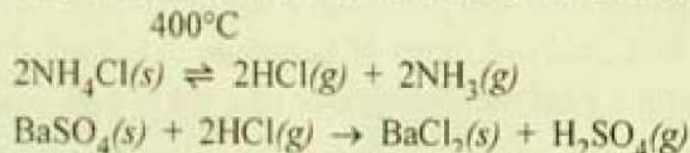
10.8 Detection of barium sulfate in pigments and paper ash

Barium sulfate is largely used as a base chemical for absorption of coal-tar dye stuff and as filler, or, extender for enamel paints. It constitutes the weighting material in the production of special papers. It is also employed in pottery, leather, rubber and dye-stuff industries. The white pigment obtained by coprecipitating barium sulfate with zinc sulfide is known as *lithopone*, which is extensively used as a non-poisonous substitute of *white lead*. Barium sulfate itself is used in the synthesis of lakes, as a white pigment in paints and in printing inks, and in medicine. Because of its radiopacity it is also used in X-ray diagnosis.

Barium sulfate can be easily detected in the pigment, or, paper ash by sodium rhodizonate test after converting it into barium chloride, according to the following procedure.

Procedure

Take a small quantity (~0.1 g) of the pigment or, the paper ash and nearly four times its bulk of very pure ammonium chloride in a silica crucible and heat the mixture strongly inside a **FUME CUPBOARD**. Hydrogen chloride produced due to thermal decomposition of NH_4Cl (at 400°C) reacts with barium sulfate and transforms it into barium chloride:



As the temperature (400°C) of the reaction is well above the boiling point of sulfuric acid (356°C), the latter volatilizes off leaving a residue of barium chloride. Continue heating until fumes no longer appear. Transfer the residue into a semi-micro test tube and treat with a drop of freshly prepared 0.2% solution of sodium rhodizonate. Appearance of a red to red-brown precipitate indicates the presence of barium sulfate in the sample.

10.9 Detection of traces of hydrogen sulfide (H_2S) in water samples

Hydrogen sulfide (H_2S) is a deadly poisonous gas. Although its lethal dose is same as that of hydrogen cyanide (HCN), but fortunately for us, its unpleasant odour is highly repulsive and prevents people from breathing it in dangerous amounts. In chemical laboratories, hydrogen sulfide gas should always be handled inside a **FUME CUPBOARD**. Hydrogen sulfide appears in natural water sources and in soil due to biodegradation of living matters. H_2S is released in the transformation of sulfur containing amino acids, viz, cysteine and cystine into pyruvic acid and decomposition of iron-sulfur proteins, ferredoxins. Some photosynthetic micro organisms, however, use H_2S in place of H_2O . Like hydrogen cyanide, traces of hydrogen sulfide may block the respiratory electron transport chain by preventing the reoxidation *cytochrome*

C oxidase bound copper (I) to copper (II) by oxygen. Therefore, detection of hydrogen sulfide in natural water, soil and air samples is very important.

Catalysis of iodine-azide reaction (Sect. 5.7) is the most suitable test for detection of traces of hydrogen sulfide in water samples. The sensitivity of the test is greatly increased by localizing the hydrogen sulfide within a small volume. This may be accomplished by shaking a large volume of water with a drop of mercury, which reacts with even traces of H_2S to produce a thin film of mercury sulfide, that remains fixed on the surface of the mercury drop. The thin film of mercury sulfide, although not visible, but it is sufficient to discharge the iodine colour with evolution of nitrogen gas from a iodine-azide solution.

Procedure

Take ~10-15 ml of sample water in a small stoppered bottle, add a drop of mercury, stopper the bottle and shake vigorously for ~10 minutes. Pour off the water and place the mercury drop on a porcelain dish or, in a depression of a spot plate. Add 1-2 drops of iodine-sodium azide reagent solution and stir with a glass rod. The thin film of mercury sulfide at once reacts with evolution of nitrogen gas. Some bubbles of N_2 gas adhere to the surface of the mercury drop and are clearly visible with the aid of magnifying glass, although the iodine colour may not be completely discharged by the trace amount of sulfide.

If necessary, several portions of the sample water may be shaken with the same drop of mercury to concentrate the mercury sulfide film, before subjecting it to the iodine-azide reaction.

Limit of identification: 0.05γ of H_2S

Limit of dilution: 1 : 2×10^8

10.10 Detection of fluoride in mineral water and rocks

Fluorine is an essential ultra trace element. 2 ppm of fluoride in diet is essential for optimal growth. It strengthens teeth in mammals and is used as CaF_2 in some molluscs. CaF_2 dramatically cuts risk of tooth decay in children. Fluoride interacts with tooth enamel, hardens it, and makes it less susceptible to decay. Fluoride deficiency makes people more prone to tooth decay. But fluoride is moderately toxic. Fluoridization of public water is not recommended, as inflammation of gums, or, gingivitis and fluorosis are common complaints. Fluoride present in superphosphate fertilizer, in mineral water and rocks are the common sources of fluoride toxicity. Therefore, detection and also estimation of fluoride content of mineral water, rock phosphates, fertilizers, etc. are extremely important.

Silicon tetrafluoride-molybdate-benzidine blue test for fluoride (*cf.* Sect 5.10) is the most suitable test for detection of traces of fluoride in mineral water and rocks.

(i) Fluoride in mineral water

Take 5 ml of the sample water in a platinum crucible add a small amount (~0.2g) of powdered quartz sand, or, silica and evaporate the mixture to dryness. If the sample water contains large amounts of other halides (*viz.* Cl^- , Br^- , I^-), add 5 ml of saturated solution of silver sulfate to precipitate these halides completely. Filter off the precipitate, if any, and

evaporate the filtrate to dryness with the quartz sand, or, silica as before. Moisten the dried residue with 1-2 drops of conc. H_2SO_4 and heat gently on an asbestos board inside a **FUME CUPBOARD**. Hold a drop of water at the head of a dropper to the issuing vapour. The water drop turns opaque if F^- is present. Subject the opaque drop to SiF_4 -molybdate-benzidine blue test, as described before (cf. Sect 5.10, 5.21).

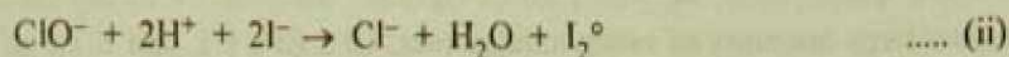
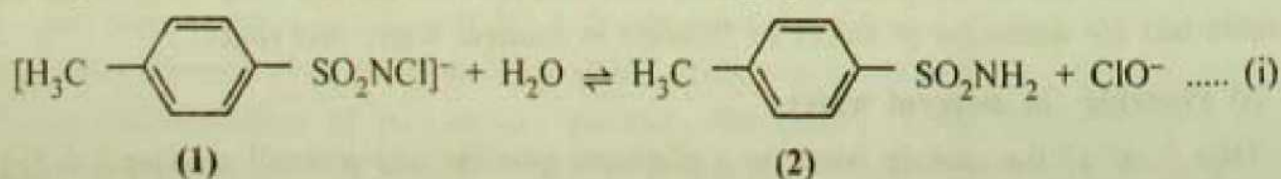
(ii) Fluoride in rock samples

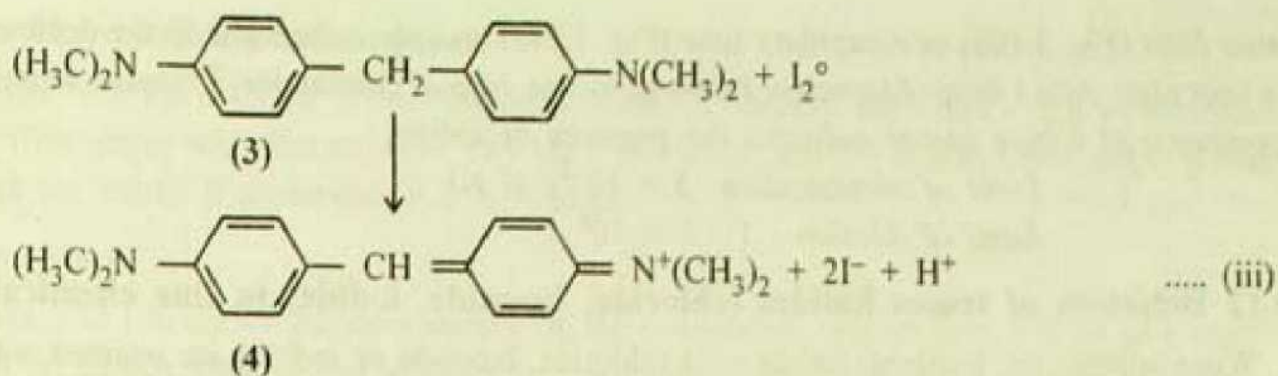
Take ~0.2 g of the powdered rock sample in a platinum crucible, add some silica and a few drops of conc. H_2SO_4 . Heat the mixture gently inside a **FUME CHAMBER** and absorb the issuing gas in a drop of water at the head of a dropper. If the rock sample already contains silica, then the addition of extra silica is not required. The water drop becomes opaque if fluoride is present. Subject the opaque drop to SiF_4 -molybdate-benzidine blue test. Otherwise, fuse the dry residue with Na_2CO_3 on a platinum wire loop, extract the molten mass with water and subject a drop of this extract to molybdenum blue-benzidine blue test described before (cf. Sect. 5.10, 5.21).

10.11 Detection of traces of iodine in sea water and mineral water samples

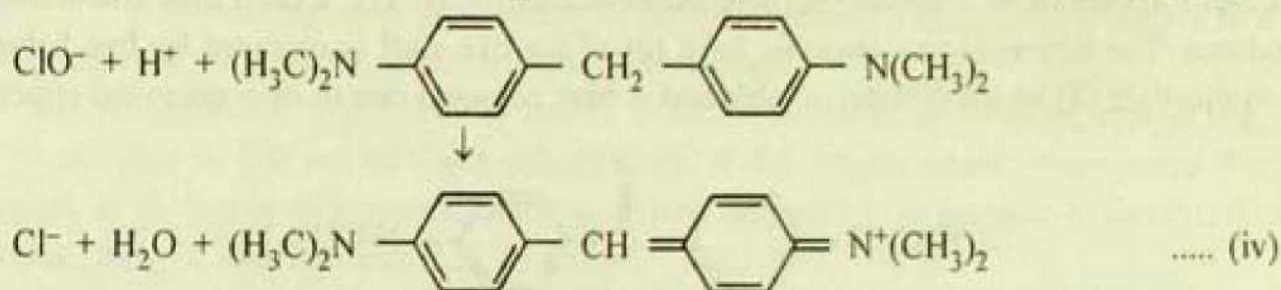
Iodine is one of the biologically essential ultra trace elements. Iodine enables the thyroid gland to biosynthesize thyroxine, an essential amino acid, which is a vitally important hormone that regulates metabolism in all the body cells. Regular dietary intake (RDI) of iodine for adult men and women are around 150 and 120 micrograms respectively. In developed countries, specified amounts of iodine or, iodide salts are added to table salts mainly as a safeguard against thyroid enlargement (*goitre*) and the severe form of mental retardation called *cretinism*, caused due to iodine deficiency. However, too much excess (>30 times of the RDI amount) of iodine may cause such deleterious effects, as, experience of metallic taste, mouth sores, diarrhoea, vomiting, headache, swollen salivary gland, acne and breathing problem. The richest natural source of iodine is *Tasmanian Wakame* (sea weed). Coastal area soils are also rich in iodine compounds, so are the dairy products from cows grazing in such soils, fruits and vegetables grown in those areas. Sea fishes are also a major source of iodine. Therefore, detection of iodine levels in sea water and in mineral water is of utmost importance.

Catalytic effect of iodide ion on the otherwise slow oxidation of colourless tetrabase (3) to its blue coloured quinoidal oxidation product (4) by hypochlorite (ClO^-) ion, generated by the hydrolysis of chloramine-T (sodium *p*-toluenesulfoncholoramide) anion (1) to the corresponding sulfonamide (2), forms the basis of this highly sensitive test.





Although, I_2 formed from the oxidation of iodide by ClO^- ion, actually oxidizes (3) to (4), but the net reaction (iv), obtained by summing up the reactions (ii) and (iii), does not involve any iodine, or, iodide and represents the equation of the uncatalysed reaction,



This indicates that iodide ion catalyses the redox reaction between chloramin-T and tetrabase.

Reagents

(i) Tetrabase solution

Take ~10 ml of 1M acetic acid in a small beaker, heat gently on a hot water bath. Add tetrabase in small portions with stirring until some tetrabase remains undissolved. Cool to room temperature, use the clear supernatant liquid (filtration is not required). Use the freshly prepared solution for the test.

(ii) Chloramin-T

Freshly prepared 1% solution in water.

Procedures

(i) Take 1 drop of the neutral test solution in a depression of a spot plate, add 1 drop of tetrabase and 1 drop of chloramin-T reagent. Mix with a glass rod. A blue colour appears immediately, or, within a few seconds depending upon the amount of iodide present. The blue colour is not permanent, it changes to green within a few minutes.

(ii) To one drop of sea water in a semi-micro test tube add 5 ml of distilled water. To the resulting mixture, add 1 drop of tetrabase and 1 drop of chloramin-T reagent solutions. A blue colour appears if iodide is present.

(iii) In a semi-micro test tube, mix 1 drop of the sample water with a grain of MgCO_3 and heat the mixture strongly. Cool to room temperature and add 2-3 drops of distilled water to the residue to dissolve the soluble iodide salt. Collect the clear liquid with the aid of a

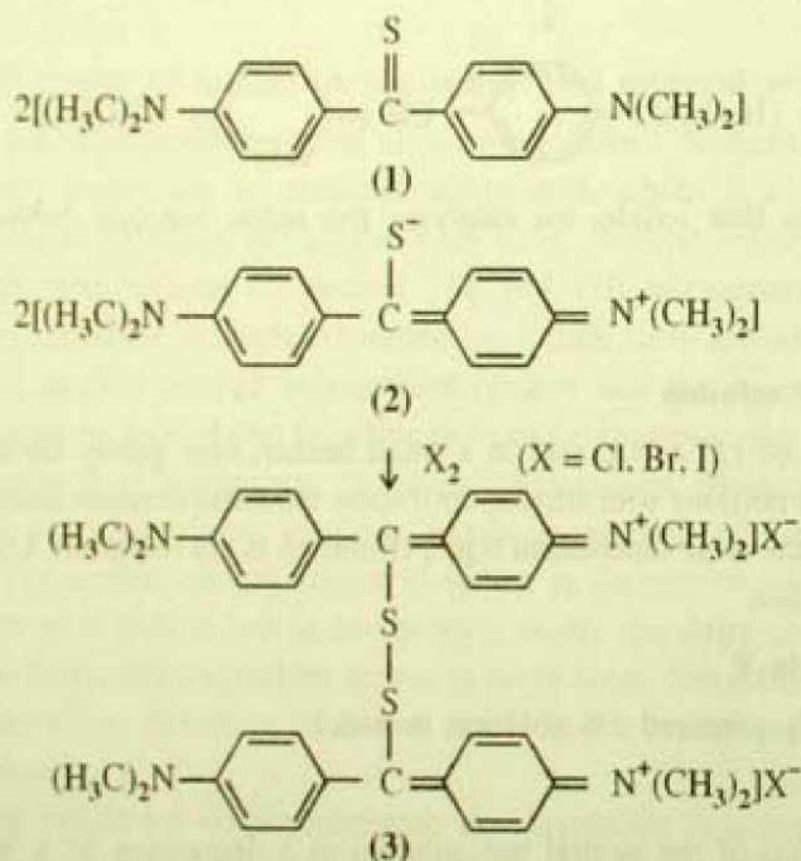
cotton filter (Fig. 3.19b) or a capillary tube (Fig. 3.24d) and place the same in the depression of a spot plate. Add 1 drop of tetrabase followed by one drop of chloramine-T reagent solutions. Appearance of a blue colour indicates the presence of iodine.

Limit of identification: $5 \times 10^{-4} \gamma$ of KI

Limit of dilution : 1 : 1×10^8

10.12 Detection of traces halides (chloride, bromide, iodide) in fine chemicals

When soluble, or, insoluble halide salts (chloride, bromide or iodide) are warmed with a mixture of chromic acid and sulfuric acid, free halogens are given off (with chloride salt, chromyl chloride CrO_2Cl_2 is also produced) (*cf.* Sects. 5.11-5.13). When dilute solutions of chlorine, bromine, or, iodine are allowed to react with the yellow coloured solution of thio Michler's ketone (4, 4' - *bis*-dimethylaminothiobenzophenone) (1), a deep blue colouration is produced. The tautomeric zwitterionic form (2) of the dye stuff is oxidized by free halogens to its disulfide (3) which is water soluble and is blue coloured due to its *p*-quinoidal structure.



The test solution should be free from other oxidizing agents, viz, nitrite, nitrous acid, nitrogen dioxide etc. Hydrogen peroxide, or, peroxodisulfate does not interfere. The test may also be applied to detect halogens in the gas phase (*cf.* Fig. 3.29), using the reagent solution, or, a filter paper impregnated with the reagent.

Reagents

(i) Chromic acid - sulfuric acid mixture

Kep a saturated solution of potassium dichromate in concentrated sulfuric acid on a boiling water bath for ~30 minutes to remove any traces of halogen that may be present in these chemicals.

(ii) Thio-Michler's ketone paper

Prepare a 0.1% solution of thio-Michler's ketone in benzene and soak a strip of Whatman No. 1 filter paper with this solution. Dry the paper in air and cut it into small strips. It may be kept for weeks if preserved in a dark place.

Procedure

Take 5 to 100 mg of the solid sample or, the evaporation residue from 1-2 ml of a nearly neutral or, weakly alkaline test solution in a semi-micro test tube. Add 3-4 drops of chromic acid-sulfuric acid mixture using a capillary dropper, avoiding contact with the wall of the test tube. Plug the mouth of the test tube with a piece of clean cotton wool and place a disc of reagent paper over its mouth (Fig. 3.27 a or b). Place the test tube inside a boiling water bath (Fig. 3.15). Depending upon the quantity of halogen present, a more or less intense blue colour appears on the reagent paper in about 1-4 minutes.

By this procedure it is possible to detect $6 \times 10^{-5}\%$ chlorine in 5 ml of conc. H_2SO_4 , $5 \times 10^{-4}\%$ chlorine in 100 mg of water soluble salts. If the reagent paper, impregnated with the reagent, is spotted with aqueous solutions of free halogens, it is possible to detect : 0.2γ of chlorine, 0.2γ of bromine and 0.5γ of iodine.

10.13 Detection of uranium in minerals

Uranium is used in nuclear reactors for generation of nuclear energy. Therefore, search for natural sources of uranium in minerals and ores is carried out regularly in geochemical and minerological explorations. Potassium ferrocyanide test and rhodamine-B test (cf. Sect. 8.10) may be applied for the detection of trace quantities of uranium in minerals and ores. Uranium minerals are very often associated with titanium, iron and other base metals which give coloured precipitates with ferrocyanide solution. These metals should be removed before testing for uranium.

Procedure

Take a minute quantity of the powdered sample and fuse the same with anhydrous Na_2CO_3 or K_2CO_3 on a platinum wire loop by heating in the Bunsen flame (cf. Sect 6.8). Cool the molten bead, take it up with 1-2 drops of conc. HCl in a small platinum crucible lid and evaporate to dryness. Cool and moisten the residue with a drop of HCl and wash down the resulting liquid into a semi-micro test tube with the aid of a few drops of water. Add a crystal of NH_4Cl , heat to boiling and add drops of *aq*- NH_3 until ammoniacal. Centrifuge and discard the centrifugate. Dissolve the precipitate in 1-2 drops of 2M HCl , add 1-2 drops of 30% H_2O_2 and drops of 2.5 M NaOH until alkaline. Boil for ~5 minutes, adding drops of water as required to replenish the reduction in volume of the solution. Centrifuge. Discard the precipitate, which may contain the hydroxides, or, hydrous oxides of titanium, zirconium, cerium, thorium manganese and iron. The centrifugate may contain CrO_4^{2-} , $\text{Al}(\text{OH})_4^-$, $\text{U}_2\text{O}_7^{2-}$ and VO_3^- . Acidify the centrifugate with dilute (~2 M) HNO_3 and add drops of BaCl_2 solution, followed by a few crystals of ammonium acetate, warm gently. Centrifuge and discard the precipitate

if any, which may be BaCrO_4 (yellow), and or, $\text{Ba(VO}_3)_2$. The centrifugate may contain UO_2^{2+} , Al^{3+} and excess Ba^{2+} ions. Add a few drops of saturated solution of $(\text{NH}_4)_2\text{CO}_3$ and warm gently for ~5 minutes. Centrifuge and discard the precipitate, which contains BaCO_3 and Al(OH)_3 if present. The centrifugate now contains only $[\text{UO}_2(\text{CO}_3)^{4-}]$, which maybe subjected to tests for uranium.

Evaporate the centrifugate to a small volume, acidify with 1-2 drops of 2M HCl and perform the following tests:

(i) **Potassium ferrocyanide test:** Place a drop of the weakly acidic test solution on a drop reaction paper impregnated with 3% solution of $\text{K}_4[\text{Fe(CN)}_6]$. According to the amount of uranium present, a more, or, less brown stain is produced.

(ii) **Rhodamine-B test:** Take 1-2 drops of the test solution on a semi-micro test tube, add drops of very dilute *aq*- NH_3 to have a just neutral or, very weakly acidic solution (test with a pH paper). Add 5 drops of the rhodamine B-benzoic acid-benzene reagent solution (0.5% solution of benzoic acid in benzene containing an excess of rhodamine-B, *cf.* Sect. 8.10) and shake vigorously. A red to pink benzene layer results if uranium is present.

10.14 Detection of gold in alloys and coatings

Gold, because of its shiny and glittering appearance, is used in making ornaments. Gold coatings are given to ornaments made of other metals and alloys, artefacts and sculptures for beautification. Since gold is a very costly and precious metal, it is often necessary to test the presence of gold in these materials without causing any visible damage to the specimens.

A rapid and sensitive test for detection of trace amounts of gold is based on the colour reaction of gold in the form of $[\text{AuCl}_4^-]$, or, $[\text{AuBr}_4^-]$ ion with rhodamine-B in benzene medium. The reaction is similar to those of $[\text{TlCl}_4^-]$ or $[\text{TlBr}_4^-]$ with rhodamine-B described in the detection of thallium in water (*cf.* Sect. 10.5).

Procedure

Draw the sample (article) over a piece of unglazed porcelain, or, over the unglazed part of the bottom of an evaporating dish, so that a hair-line scratch is formed on the porcelain. Now with the aid of a capillary dropper, spot the scratch with a drop of bromine-hydrochloric acid mixture (i.e. a mixture of equal volumes of bromine-water and concentrated hydrochloric acid) to oxidize metallic gold to Au^{III} -halo complexes, $[\text{AuCl}_4^-]$ and/or $[\text{AuBr}_4^-]$ ions and Cr^{III} if any, to Cr^{VI} by hypobromite. Wait for 2-3 minutes. Add one drop of 10% aqueous solution of sulfosalicylic acid to consume the excess bromine (in the form of soluble colourless bromosulfosalicylic acid, (*cf.* Sect. 4.13). Now wash down the resulting liquid into a micro test tube, add drops of water if necessary with the aid of a capillary dropper. Add one drop of 0.2% aqueous solution of rhodamine-B reagent and 5-6 drops of benzene, shake the mixture vigorously and expose the mixture to *uv*-radiation for a few minutes. If gold is present, the red benzene layer shows an orange fluorescence.

Limit of identification: 0.1γ of Au

Limit of dilution: 1 : 5×10^5

Appendix

Appendix-A1

Acidity Constants (pK_n^H) of Some Inorganic Acids at 25°C.

(Relevant to qualitative inorganic analysis)

Deprotonation equilibria : $H_nA \rightleftharpoons H_{n-1}A^- + H^+$

$$K_n^H = ([H^+][H_{n-1}A^-]) / [H_nA]$$

$$pK_n^H = -\log_{10} K_n^H$$

Name of acid	Acid	Conjugate base	pK_n^H
Ammonium ion	NH_4^+	NH_3	9.2
Antimonous acid	$HSbO_2$	SbO_2^-	11
Arsenic acid	H_3AsO_4	$H_2AsO_4^-$	2.3 – 3.6
	$H_2AsO_4^-$	$HAsO_4^{2-}$	6.8 – 7.2
	$HAsO_4^{2-}$	AsO_4^{3-}	12.0 – 12.5
Arsenious acid	$HAsO_2$	AsO_2^-	9.2
Boric acid	H_3BO_3	$B(OH)_4^-$	9.2
Carbonic acid	$(CO_2 + H_2O)$	HCO_3^-	6.4
	HCO_3^-	CO_3^{2-}	10.2
Chromic acid	H_2CrO_4	$HCrO_4^-$	0.7
	$HCrO_4^-$	CrO_4^{2-}	6.5
Cyanic acid	$HCNO$	CNO^-	3.9
Hydrazoic acid	HN_3	N_3^-	4.7
Hydrazinium ion	$H_2NNH_3^+$	H_2NNH_2	7.9
Hydrocyanic acid	HCN	CN^-	9.4
Hydrofluoric acid	HF	F^-	3.2
Hydrogen peroxide	H_2O_2	HO_2^-	11.7 (20°C)
Hydroselenic acid	H_2Se	HSe^-	3.7 – 3.8
Hydrosulfuric acid	H_2S	HS^-	7.1
	HS^-	S^{2-}	13.0
Hydrosulfurous acid	$HS_2O_4^-$	$S_2O_4^{2-}$	2.5

Appendix-A1 (Continued)

Name of acid	Acid	Conjugate base	pK_a^H
Hydrotelluric acid	H_2Te	HTe^-	2.6 - 2.7
Hydroxylammonium ion	NH_3^+OH	NH_2OH	6
Hypochlorous acid	$HOCl$	OCl^-	7.4
Nitrous acid	HNO_2	NO_2^-	3.3-3.4
Periodic acid	H_5IO_6	$H_4IO_6^-$	3.3
	$H_4IO_6^-$	$H_3IO_6^{2-}$	6.7
Phosphoric acid	H_3PO_4	$H_2PO_4^-$	2.1
	$H_2PO_4^-$	HPO_4^{2-}	7.2
	HPO_4^{2-}	PO_4^{3-}	12.3
Phosphorous acid	H_3PO_3	$H_2PO_3^-$	1.5 - 1.8
	$H_2PO_3^-$	HPO_3^{2-}	6.2 - 6.6
Selenous acid	H_2SeO_3	$HSeO_3^-$	2.6
	$HSeO_3^-$	SeO_3^{2-}	8.3
Sulfuric acid	HSO_4^-	SO_4^{2-}	1.9
Sulfurous acid	$(SO_2 + H_2O)$	HSO_3^-	1.8
	HSO_3^-	SO_3^{2-}	7.1-7.3
Telluric acid	H_6TeO_6	$H_5TeO_6^-$	6.2 - 8.8
	$H_5TeO_6^-$	$H_4TeO_6^{2-}$	10.4
Tellurous acid	H_2TeO_3	$HTeO_3^-$	2.7
	$HTeO_3^-$	TeO_3^{2-}	8.0
Thiosulfuric acid	$H_2S_2O_3$	$HS_2O_3^-$	0.3 - 1.2
	$HS_2O_3^-$	$S_2O_3^{2-}$	1.5
Water (hydronium ion)	H_3O^+	H_2O	-1.7 (?)
	H_2O	OH^-	15.7 (?)
	OH^-	O^{2-}	24-36 (Ca)



Appendix-A2

Acidity Constants (pK_a^H) of Some Organic Acids at 25°C

Name of acid	Acid	Conjugate base	pK_a^H
Acetic acid	CH_3COOH	CH_3COO^-	4.8
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH}$	$\text{C}_6\text{H}_5\text{COO}^-$	4.7
Anilinium ion	$\text{C}_6\text{H}_5\text{NH}_3^+$	$\text{C}_6\text{H}_5\text{NH}_2$	4.6
Citric acid	$(\text{C}_3\text{H}_5\text{O})(\text{COOH})_3$	$(\text{C}_3\text{H}_5\text{O})(\text{COOH})_2(\text{COO}^-)$	3.1
	$(\text{C}_3\text{H}_5\text{O})(\text{COOH})_2(\text{COO}^-)$	$(\text{C}_3\text{H}_5\text{O})(\text{COOH})(\text{COO}^-)_2$	4.8
	$(\text{C}_3\text{H}_5\text{O})(\text{COOH})(\text{COO}^-)_2$	$(\text{C}_3\text{H}_5\text{O})(\text{COO}^-)_3$	6.7
Formic acid	HCOOH	HCOO^-	3.7
Hexamethylenetetra ammonium ion	$(\text{CH}_2)_6\text{N}_4\text{H}^+$	$(\text{CH}_2)_6\text{N}_4$	4.9
Monochloroacetic acid	ClCH_2COOH	$\text{ClCH}_2\text{COO}^-$	2.9
Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4$	HC_2O_4^-	1.2
	HC_2O_4^-	$\text{C}_2\text{O}_4^{2-}$	4.3
Phenol	$\text{C}_6\text{H}_5\text{OH}$	$\text{C}_6\text{H}_5\text{O}^-$	9.9
Phthalic acid	$\text{C}_6\text{H}_4(\text{COOH})_2$	$\text{C}_6\text{H}_4(\text{COOH})(\text{COO}^-)$	2.9
	$\text{C}_6\text{H}_4(\text{COOH})(\text{COO}^-)$	$\text{C}_6\text{H}_4(\text{COO}^-)_2$	5.1
Picric acid	$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$	$\text{C}_6\text{H}_2(\text{NO}_2)_3\text{O}^-$	0.4
Salicylic acid	$\text{C}_6\text{H}_4(\text{OH})(\text{COOH})$	$\text{C}_6\text{H}_4(\text{OH})\text{COO}^-$	3.0
	$\text{C}_6\text{H}_4(\text{OH})(\text{COO}^-)$	$\text{C}_6\text{H}_4(\text{O}^-)(\text{COO}^-)$	14.4
Sulfanilic acid	$\text{H}_3\text{N}^+\text{C}_6\text{H}_4\text{SO}_3^-$	$\text{H}_2\text{N.C}_6\text{H}_4.\text{SO}_3^-$	3.2
Tartaric acid	$(\text{CHOH})_2(\text{COOH})_2$	$(\text{CHOH})_2(\text{COOH})(\text{COO}^-)$	3.0
	$(\text{CHOH})_2(\text{COOH})(\text{COO}^-)$	$(\text{CHOH})_2(\text{COO}^-)_2$	4.5



Appendix-A3

First Acid Dissociation Constants of Some Hydrated Metal Ions at 25°C

Acid dissociation equilibria : $M^{n+}(aq) \rightleftharpoons M^{(n-1)+}(aq) + H^+(aq)$

$$K_M^H = \frac{[M^{(n-1)+}(aq)][H^+(aq)]}{[M^{n+}(aq)]}$$

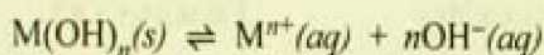
$$pK_M^H = -\log_{10} K_M^H$$

$M^{n+}(aq)$	pK_M^H	$M^{n+}(aq)$	pK_M^H
$Fe^{3+}(aq)$	2.20	$Co^{2+}(aq)$	8.89
$Cr^{3+}(aq)$	3.80	$Fe^{2+}(aq)$	9.49
$Al^{3+}(aq)$	4.85	$Zn^{2+}(aq)$	9.60
$Be^{2+}(aq)$	6.52	$Ni^{2+}(aq)$	10.60

Appendix-A4

Solubility Products of Some Metal Hydroxides at 25°C

Solubility equilibria:



$$K_{sp} = [M^{n+}(aq)][OH^-(aq)]^n$$

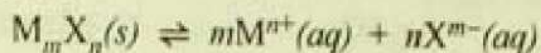
$$pK_{sp} = -\log K_{sp}$$

M^{n+}	pK_{sp}	M^{n+}	pK_{sp}	M^{n+}	pK_{sp}
Ag^+	7.7	Cu^+	14.9	Sn^{2+}	26.5-27
Al^{3+}	32.3	Cu^{2+}	18.2-19.2	Sn^{4+}	~56
Au^+	19.1	Fe^{2+}	15.3	Th^{4+}	39.0
Au^{3+}	44.1	Fe^{3+}	37.2-38.2	Ti^{3+}	35-40
Ba^{2+}	2.3	Hg^{2+}	25.5	TiO^{2+}	$2OH^-$ (~29)
Be^{2+}	20-26	Mg^{2+}	11.0	Tl^+	0.2
Bi^{3+}	$(1 OH^-)$ 11-12	Mn^{2+}	12.5-12.8	Tl^{3+}	45.2
Ca^{2+}	5.1	Mn^{3+}	36	U^{3+}	19
Cd^{2+}	14.2	Mn^{4+}	56	U^{4+}	45
Ce^{3+}	19.8-21.8	Ni^{2+}	18.1	UO_2^{2+}	$(2OH^-)$ 22.7
Ce^{4+}	54.8	Pb^{2+}	14.4 - 15.6	VO_2^+	$(1OH^-)$ 14.1
Co^{2+}	15.6	Pb^{4+}	64-65.5	Zn^{2+}	16.9
Co^{3+}	42.6	Pd^{2+}	31.0	ZrO^{2+}	$(2OH^-)$ 25.5
Cr^{2+}	17.0	Sb^{3+}	$(1OH^-)$ 17.1	VO^{2+}	$(2OH^-)$ 22.1
Cr^{3+}	30.3	Sr^{2+}	3.5		



Appendix-A5

Solubility Products (K_{sp}) of Some Sparingly Soluble Salts M_mX_n at 25°C
Solubility equilibria:

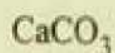


$$K_{sp} = [M^{n+}(aq)]^m[X^{m-}(aq)]^n$$

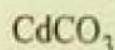
Halides/Oxyhalides/Pseudohalides



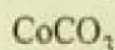
Carbonates



$$5 \times 10^{-9}$$



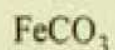
$$6.2 \times 10^{-12}$$



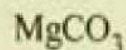
$$1.4 \times 10^{-13}$$



$$2.5 \times 10^{-10}$$



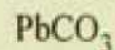
$$3.47 \times 10^{-11}$$



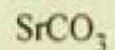
$$2.2 \times 10^{-11}$$



$$1.3 \times 10^{-7}$$



$$7.5 \times 10^{-14}$$

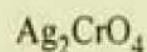


$$5.6 \times 10^{-10}$$

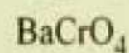


$$1.2 \times 10^{-10}$$

Chromates



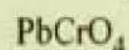
$$1.1 \times 10^{-12}$$



$$1.2 \times 10^{-10}$$



$$7.1 \times 10^{-4}$$



$$2.8 \times 10^{-13}$$

Sulfides



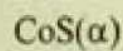
$$6.3 \times 10^{-50}$$



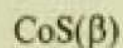
$$1 \times 10^{-97}$$



$$7.9 \times 10^{-27}$$



$$4.0 \times 10^{-21}$$



$$2.0 \times 10^{-25}$$



$$6.3 \times 10^{-36}$$



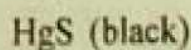
$$2.5 \times 10^{-48}$$



$$5 \times 10^{-18}$$



$$1 \times 10^{-47}$$



$$1.6 \times 10^{-52}$$

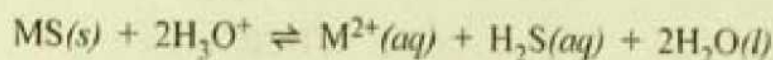
Appendix-A5 (Continued)

HgS (red)	4×10^{-53}	UO ₂ HPO ₄	2.14×10^{-11}
MnS (flesh coloured)	2.5×10^{-10}	<i>Sulfates/Sulfites</i>	
MnS (green)	2.5×10^{-13}	Ag ₂ SO ₄	1.2×10^{-5}
NiS (α)	3.2×10^{-19}	Ag ₂ SO ₃	1.5×10^{-14}
NiS (β)	1×10^{-24}	BaSO ₄	1.1×10^{-10}
NiS (γ)	2×10^{-26}	CaSO ₄	7.1×10^{-5}
PbS	2.5×10^{-27}	PbSO ₄	1.8×10^{-8}
Sb ₂ S ₃	1.6×10^{-93}	SrSO ₄	3.2×10^{-7}
SnS	1×10^{-25}	<i>Ferrocyanides/ Ferricyanides</i>	
ZnS (α)	1.6×10^{-24}	Ag ₄ [Fe(CN) ₆]	1.5×10^{-41}
ZnS (β)	2.5×10^{-22}	Ag ₃ [Fe(CN) ₆]	1×10^{-22}
<i>Phosphates</i>		Ba ₂ [Fe(CN) ₆]	3×10^{-8}
Ag ₃ PO ₄	1.3×10^{-20}	Cu ₂ [Fe(CN) ₆]	1.3×10^{-16}
AlPO ₄	5.75×10^{-19}	Fe ₄ [Fe(CN) ₆] ₃	3×10^{-41}
Ba ₃ (PO ₄) ₂	6.03×10^{-39}	Ni ₂ [Fe(CN) ₆]	1.3×10^{-15}
BiPO ₄	1.3×10^{-23}	Pb ₂ [Fe(CN) ₆]	3.5×10^{-15}
CaHPO ₄	2.7×10^{-7}	(UO ₂) ₂ [Fe(CN) ₆]	7.0×10^{-14}
Ca ₃ (PO ₄) ₂	2.1×10^{-33}	Zn ₂ [Fe(CN) ₆]	4.1×10^{-16}
CrPO ₄ (green)	$\sim 2.5 \times 10^{-23}$	<i>Oxalates/Cobaltinitrites</i>	
CrPO ₄ (violet)	$\sim 1 \times 10^{-17}$	Ag ₂ C ₂ O ₄	3.5×10^{-11}
Cu ₃ (PO ₄) ₂	1.7×10^{-37}	BaC ₂ O ₄	1.1×10^{-7}
FePO ₄	1.3×10^{-22}	CaC ₂ O ₄	2.3×10^{-9}
Mg ₃ (PO ₄) ₂	1×10^{-13}	Fe(C ₂ O ₄)	2×10^{-7}
NH ₄ MgPO ₄	2.5×10^{-13}	MgC ₂ O ₄	8.6×10^{-5}
Pb ₃ (PO ₄) ₂	7.9×10^{-33}	NiC ₂ O ₄	4×10^{-10}
Sr ₃ (PO ₄) ₂	6.03×10^{-37}	PbC ₂ O ₄	4.8×10^{-10}
Zn ₃ (PO ₄) ₂	9.1×10^{-33}	SrC ₂ O ₄	5.6×10^{-8}
Th ₃ (PO ₄) ₄	2.57×10^{-79}	K ₃ [Co(NO ₂) ₆]	4.3×10^{-10}
Zr ₃ (PO ₄) ₄	1.2×10^{-132}	K ₂ Na[Co(NO ₂) ₆]	2.2×10^{-11}
NH ₄ UO ₂ PO ₄	4.4×10^{-27}	(NH ₄) ₃ [Co(NO ₂) ₆]	7.6×10^{-6}

Appendix-A6

Solubility Products in Acid (K_{spa}) of Some Metal Sulfides at 25°C

Solubility equilibria in acid:



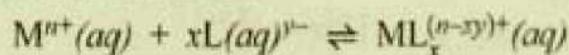
$$K_{spa} = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2}$$

<i>Metal sulfide (formula)</i>	<i>K_{spa}</i>
Cadmium sulfide (CdS)	8×10^{-7}
Cobalt (II) sulfide (CoS)	4×10^{-1}
Copper (II) sulfide (CuS)	6×10^{-16}
Iron (II) sulfide (FeS)	6×10^2
Lead(II) sulfide (PbS)	3×10^{-7}
Manganese(II) sulfide (MnS)	3×10^{10}
Mercury (II) sulfide (HgS)	2×10^{-32}
Nickel (II) sulfide (NiS)	8×10^{-1}
Silver (I) sulfide (Ag ₂ S)	6×10^{-30}
Tin (II) sulfide (SnS)	1×10^{-5}
Zinc sulfide (ZnS)	3×10^{-2}

Appendix-A7

Overall Stability Constants ($\log \beta$) of Some Metal Complexes with Common Ligands at 25°C

Overall complex formation equilibria:



$$\beta = \frac{[ML_x^{(n-xy)+}(aq)]}{[M^{n+}(aq)][L(aq)^{y-}]^x}$$

(* Neutral molecular complexes in solution are indicated by asteric mark).

Ammine complexes:

		$[Co(NH_3)_6]^{2+}$	4.39
$[Ag(NH_3)_2]^+$	7.24	$[Cu(NH_3)_2]^+$	10.86
$[Cd(NH_3)_4]^{2+}$	6.56	$[Cu(NH_3)_4]^{2+}$	12.03
$[Co(NH_3)_6]^{3+}$	35.21	$[Hg(NH_3)_4]^{2+}$	19.3

Appendix-A7 (Continued)

$[\text{Ni}(\text{NH}_3)_6]^{2+}$	8.70	$[\text{PbCl}_3^-]$	2.04
$[\text{Zn}(\text{NH}_3)_4]^{2+}$	8.70	$[\text{SnCl}_4]^{2-}$	1.48
<i>Fluoro complexes</i>		$[\text{TiCl}_5]^{2-}$	17.47
$[\text{AlF}_6]^{3-}$	20.67	$[\text{PdCl}_6]^{4-}$	11.3
$[\text{BeF}_4]^{2-}$	16.38	$[\text{PdCl}_4]^{2-}$	15.5
$[\text{FeF}_6]^{3-}$	~16.10	<i>Cyano complexes</i>	
$[\text{TiOF}_4]^{2-}$	17.5	$[\text{Ag}(\text{CN})_2^-]$	19.45
$[\text{UO}_2\text{F}_4]^{2-}$	11.7	$[\text{Ag}(\text{CN})_4]^{3-}$	19.42
$[\text{VOF}_3^-]$	7.2	$[\text{Cd}(\text{CN})_4]^{2-}$	17.11
$[\text{ZrF}_3^+]$	23.45	$[\text{Cu}(\text{CN})_4]^{3-}$	30.30
<i>Hydroxo complexes</i>		$[\text{Fe}(\text{CN})_6]^{4-}$	24.0
$[\text{Al}(\text{OH})_4^-]$	33.0	$[\text{Fe}(\text{CN})_6]^{3-}$	31.0
$[\text{Bi}(\text{OH})_4^-]$	35.2	$[\text{Hg}(\text{CN})_4]^{2-}$	41.51
$[\text{Cu}(\text{OH})_4]^{2-}$	18.5	$[\text{Ni}(\text{CN})_4]^{2-}$	31.0
$[\text{Fe}(\text{OH})_4]^{2-}$	8.56	$[\text{Zn}(\text{CN})_4]^{2-}$	19.0
$[\text{Pb}(\text{OH})_3^-]$	13.3	<i>Acetato complexes ($\text{CH}_3\text{COO}^- = \text{Ac}^-$)</i>	
$[\text{Sb}(\text{OH})_4^-]$	38.3	$[\text{Cd}(\text{Ac})_2]^*$	2.28
$[\text{Sn}(\text{OH})_3^-]$	25.13	$[\text{Cd}(\text{Ac})_4]^{2-}$	2.00
$[\text{Sn}(\text{OH})_6]^{2-}$	63	$[\text{Cu}(\text{Ac})_2]^*$	3.30
$[\text{UO}_2(\text{OH})_4]^{2-}$	32.40	$[\text{Pb}(\text{Ac})_2]^*$	4.0
$[\text{VO}(\text{OH})^+]$	8.6	$[\text{Pb}(\text{Ac})_4]^{2-}$	8.5
$[\text{Zn}(\text{OH})_4]^{2-}$	14.66	$[\text{UO}_2(\text{Ac})_2]^*$	4.36
<i>Chloro complexes</i>		$[\text{UO}_2(\text{Ac})_3^-]$	6.34
$[\text{AgCl}_4]^{3-}$	5.30	<i>Tartarato complexes</i>	
$[\text{CdCl}_4]^{2-}$	2.90	$([\text{CH}(\text{OH})\text{COO}^-]_2 = \text{tta}^{2-})$	
$[\text{CuCl}_3]^{2-}$	5.63	$[\text{Cu}(\text{tta})]^*$	3.0
$[\text{CuCl}_3^-]$	- 2.1	$[\text{Cu}(\text{tta})_2]^{2-}$	5.11
$[\text{FeCl}_4^-]$	- 0.85	$[\text{Pb}(\text{tta})]^*$	3.78
$[\text{HgCl}_4]^{2-}$	15.07	$[\text{Zn}(\text{tta})]^*$	2.68
		$[\text{Fe}(\text{tta})^+]$	7.49

Appendix-A7 (Continued)

Oxalato complexes ($C_2O_4^{2-} = ox^{2-}$)

$[Al(ox)_3^{3-}]$	16.30
$[Cd(ox)_2^{2-}]$	5.77
$[Ce(ox)_3^{3-}]$	11.30
$[Co(ox)_3^{4-}]$	9.7
$[Cu(ox)_2^{2-}]$	10.3
$[Fe(ox)_3^{4-}]$	5.22
$[Fe(ox)_3^{3-}]$	20.2
$[Mn(ox)_2^{2-}]$	5.25
$[Pb(ox)_2^{2-}]$	6.54
$[Sr(ox)]^*$	2.54
$[Zn(ox)_2^{2-}]$	7.36
$[Zn(ox)_3^{4-}]$	8.15

1,10-phenanthroline (phen) complexes

$[Fe(phen)_3^{2+}]$	21.3
$[Ni(phen)_3^{2+}]$	24.8
$[Co(phen)_3^{2+}]$	19.90
$[Cu(phen)_2^{2+}]$	16.00
$[Zn(phen)_2^{2+}]$	12.15
$[Cu(phen)_3^{2+}]$	21.35

Iodo complexes

$[AgI_2^-]$	11.74
$[AgI_4^{3-}]$	13.10
$[BiI_6^{3-}]$	19.1
$[CuI_2^-]$	8.85
$[HgI_4^{2-}]$	29.83
$[PbI_4^{2-}]$	3.92
$[ZnI_4^{2-}]$	- 2.3

Thiosulfato complexes

$[Ag(S_2O_3)_2^{3-}]$	13.46
$[Cd(S_2O_3)_2^{2-}]$	6.48
$[Cu(S_2O_3)^-]$	10.27
$[Cu(S_2O_3)_2^{3-}]$	12.22
$[Cu(S_2O_3)_2^{2-}]$	12.29
$[Hg(S_2O_3)_2^{2-}]$	29.86
$[Hg(S_2O_3)_4^{6-}]$	33.61
$[Pb(S_2O_3)_2^{2-}]$	5.13
$[Pb(S_2O_3)_3^{4-}]$	6.35
$[Pb(S_2O_3)_4^{6-}]$	7.2
$[Zn(S_2O_3)_2^{2-}]$	4.59

Thiocyanato complexes

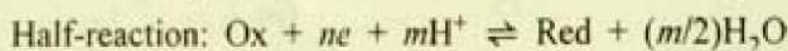
$[Ag(SCN)_2^-]$	8.23
$[Ag(SCN)_4^{3-}]$	9.67
$[Bi(SCN)_4^-]$	3.41
$[Bi(SCN)_6^{3-}]$	4.23
$[Co(SCN)_4^{2-}]$	2.2
$[Cr(SCN)_6^{3-}]$	3.8
$[Cu(SCN)_2^-]$	12.11
$[Cu(SCN)_4^{3-}]$	10.05
$[Fe(SCN)^{2+}]$	3.03
$[Fe(SCN)_3]^*$	4.63
$[Fe(SCN)_6^{3-}]$	3.23
$[Hg(SCN)_2]^*$	17.47
$[Hg(SCN)_4^{2-}]^*$	19.77
$[Cu(SCN)_2]^*$	3.65
$[Cu(SCN)_4^{2-}]$	6.52

Appendix-A7 (Continued)

<i>Phosphato complexes</i>		$[\text{Fe}(\text{H}_2\text{PO}_4)^{2+}]$	3.5
$[\text{Fe}(\text{HPO}_4)^+]$	9.75	$[\text{Fe}(\text{H}_2\text{PO}_4)_4^-]$	9.15
$[\text{Ca}(\text{HPO}_4)]^*$	2.70	$[\text{UO}_2(\text{H}_2\text{PO}_4)^+]$	3.0
$[\text{Mg}(\text{HPO}_4)]^*$	2.50	$[\text{UO}_2(\text{H}_2\text{PO}_4)_3^-]$	7.33
$[\text{Al}(\text{H}_2\text{PO}_4)^{2+}]$	3.0	$[\text{Ce}(\text{PO}_4)]^*$	18.53
$[\text{Ca}(\text{H}_2\text{PO}_4)^+]$	1.08		

Appendix-A8

Standard Reduction Potentials (E°) of Some Common Redox Couples at 25°C



$$(n \geq 1, m \geq 0)$$

$$\text{Nernst equation: } E = E^\circ + \frac{0.059}{n} \log_{10} \frac{a_{\text{Ox}}}{a_{\text{Red}}}$$

$$(a_{\text{Ox}} = a_{\text{Red}} = 1M, a_{\text{H}^+} = 1M, a_{\text{OH}^-} = 1M)$$

<i>Half-reaction</i>	<i>E° (Volt)</i>
$\text{F}_2(\text{g}) + 2e \rightarrow 2\text{F}^-(\text{aq})$	2.87
$\text{O}_3(\text{g}) + 2\text{H}^+(\text{aq}) + 2e \rightarrow \text{O}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	2.08
$\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2e \rightarrow 2\text{SO}_4^{2-}(\text{aq})$	2.01
$\text{Co}^{3+}(\text{aq}) + e \rightarrow \text{Co}^{2+}(\text{aq})$	1.81
$\text{H}_2\text{O}_2(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.76
$\text{Ce}^{4+}(\text{aq}) + e \rightarrow \text{Ce}^{3+}(\text{aq})$	1.72
$\text{MnO}_4^- + 4\text{H}^+(\text{aq}) + 3e \rightarrow \text{MnO}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	1.68
$\text{PbO}_2(\text{s}) + 3\text{H}^+(\text{aq}) + \text{HSO}_4^- + 2e \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O}(\text{l})$	1.628
$2\text{HClO}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e \rightarrow \text{Cl}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	1.61
$\text{Mn}^{3+}(\text{aq}) + e \rightarrow \text{Mn}^{2+}(\text{aq})$	1.54
$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5e \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$	1.51
$\text{ClO}_3^-(\text{aq}) + 6\text{H}^+(\text{aq}) + 5e \rightarrow (1/2)\text{Cl}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l})$	1.47
$\text{Au}^{3+}(\text{aq}) + 2e \rightarrow \text{Au}^+(\text{aq})$	1.40
$2\text{BrO}_3^-(\text{aq}) + 12\text{H}^+(\text{aq}) + 10e \rightarrow \text{Br}_2(\text{l}) + 6\text{H}_2\text{O}(\text{l})$	1.48
$\text{Cl}_2(\text{g}) + 2e \rightarrow 2\text{Cl}^-(\text{aq})$	1.36

Appendix-A8 (Continued)

$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+(\text{aq}) + 6e \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	1.33
$\text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4e \rightarrow 2\text{H}_2\text{O}(\text{l})$	1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + 2e \rightarrow \text{Mn}^{2+}(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$	1.22
$2\text{IO}_3^-(\text{aq}) + 12\text{H}^+(\text{aq}) + 10e \rightarrow \text{I}_2(\text{s}) + 6\text{H}_2\text{O}(\text{l})$	1.20
$\text{Br}_2(\text{l}) + 2e \rightarrow 2\text{Br}^-(\text{aq})$	1.09
$\text{HNO}_2(\text{aq}) + \text{H}^+(\text{aq}) + e \rightarrow \text{NO}(\text{g}) + \text{H}_2\text{O}(\text{l})$	0.98
$\text{NO}_3^-(\text{aq}) + 4\text{H}^+(\text{aq}) + 3e \rightarrow \text{NO}(\text{g}) + 2\text{H}_2\text{O}(\text{l})$	0.96
$2\text{Hg}^{2+}(\text{aq}) + 2e \rightarrow \text{Hg}_2^{2+}(\text{aq})$	0.92
$\text{HO}_2^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2e \rightarrow 3\text{OH}^-(\text{aq})$	0.88
$\text{Hg}^{2+}(\text{aq}) + 2e \rightarrow \text{Hg}(\text{l})$	0.85
$\text{ClO}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) + 2e \rightarrow \text{Cl}^-(\text{aq}) + 2\text{OH}^-(\text{aq})$	0.81
$\text{Ag}^+(\text{aq}) + e \rightarrow \text{Ag}(\text{s})$	0.80
$\text{Hg}_2^{2+}(\text{aq}) + 2e \rightarrow 2\text{Hg}(\text{l})$	0.80
$\text{NO}_3^- + 2\text{H}^+(\text{aq}) + e \rightarrow \text{NO}_2(\text{g}) + \text{H}_2\text{O}(\text{l})$	0.79
$\text{Fe}^{3+}(\text{aq}) + e \rightarrow \text{Fe}^{2+}(\text{aq})$	0.77
$\text{O}_2(\text{g}) + 2\text{H}^+(\text{aq}) + 2e \rightarrow \text{H}_2\text{O}_2(\text{aq})$	0.70
$\text{MnO}_4^-(\text{aq}) + e \rightarrow \text{MnO}_4^{2-}(\text{aq})$	0.56
$\text{H}_3\text{AsO}_4(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e \rightarrow \text{H}_3\text{AsO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.56
$\text{I}_2(\text{s}) + 2e \rightarrow 2\text{I}^-(\text{aq})$	0.54
$\text{Cu}^+(\text{aq}) + e \rightarrow \text{Cu}(\text{s})$	0.52
$\text{H}_2\text{SO}_3(\text{aq}) + 4\text{H}^+(\text{aq}) + 4e \rightarrow \text{S}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$	0.45
$\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4e \rightarrow 4\text{OH}^-(\text{aq})$	0.40
$\text{Cu}^{2+}(\text{aq}) + 2e \rightarrow \text{Cu}(\text{s})$	0.34
$\text{BiO}^+(\text{aq}) + 2\text{H}^+(\text{aq}) + 3e \rightarrow \text{Bi}(\text{s}) + \text{H}_2\text{O}(\text{l})$	0.32
$\text{Hg}_2\text{Cl}_2(\text{s}) + 2e \rightarrow 2\text{Hg}(\text{l}) + 2\text{Cl}^-(\text{aq})$	0.28
$\text{AgCl}(\text{s}) + e \rightarrow \text{Ag}(\text{s}) + \text{Cl}^-(\text{aq})$	0.22
$\text{SO}_4^{2-}(\text{aq}) + 2\text{H}^+(\text{aq}) + 2e \rightarrow \text{SO}_3^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	0.17
$\text{Cu}^{2+}(\text{aq}) + e \rightarrow \text{Cu}^+(\text{aq})$	0.15
$\text{Sn}^{4+}(\text{aq}) + 2e \rightarrow \text{Sn}^{2+}(\text{aq})$	0.15

Appendix-A8 (Continued)

$S(s) + 2H^+ + 2e \rightarrow H_2S(aq)$	0.14
$AgBr(s) + e \rightarrow Ag(s) + Br^-(aq)$	0.07
$2H^+(aq) + 2e \rightarrow H_2(g)$	0.00
$Fe^{3+}(aq) + 3e \rightarrow Fe(s)$	-0.04
$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$	-0.13
$CrO_4^{2-}(aq) + 4H_2O(l) + 3e \rightarrow Cr(OH)_3(s) + 5OH^-(aq)$	-0.13
$Sn^{2+}(aq) + 2e \rightarrow Sn(s)$	-0.14
$AgI(s) + e \rightarrow Ag(s) + I^-(aq)$	-0.15
$Ni^{2+}(aq) + 2e \rightarrow Ni(s)$	-0.26
$Co^{2+}(aq) + 2e \rightarrow Co(s)$	-0.28
$PbSO_4(s) + H^+(aq) + 2e \rightarrow Pb(s) + HSO_4^-(aq)$	-0.296
$Tl^+(aq) + e \rightarrow Tl(s)$	-0.34
$Se(s) + 2H^+(aq) + 2e \rightarrow H_2Se(aq)$	-0.40
$Cd^{2+}(aq) + 2e \rightarrow Cd(s)$	-0.40
$Cr^{3+}(aq) + e \rightarrow Cr^{2+}(aq)$	-0.41
$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	-0.45
$2CO_2(g) + 2H^+(aq) + 2e \rightarrow H_2C_2O_4(aq)$	-0.45
$Cr^{3+}(aq) + 3e \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$	-0.76
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$	-0.83
$Cr^{2+}(aq) + 2e \rightarrow Cr(s)$	-0.91
$Mn^{2+}(aq) + 2e \rightarrow Mn(s)$	-1.18
$Al^{3+}(aq) + 3e \rightarrow Al(s)$	-1.66
$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$	-2.37
$Na^+(aq) + e \rightarrow Na(s)$	-2.71
$Ca^{2+}(aq) + 2e \rightarrow Ca(s)$	-2.87
$Ba^{2+}(aq) + 2e \rightarrow Ba(s)$	-2.91
$K^+(aq) + e \rightarrow K(s)$	-2.93
$Li^+(aq) + e \rightarrow Li(s)$	-3.04



Appendix-B

Reagents used in Qualitative Inorganic Analysis

* Reagents of limited stability, should not be kept longer than one month.

\$ Reagents should be freshly prepared in small quantities and then discarded after use.

Toxic chemicals, to be handled with **CAUTION**.

Appendix-B1

Strengths of Concentrated Acids

Acids (formula)	Weight(%)	Specific gravity	Normality (N)
1. Acetic acid [glacial] (CH_3COOH)	99.5	1.05	17N
2. Hydrofluoric acid (HF)	48		27N
3. Hydrochloric acid (HCl)	38	1.19	12N
4. Hydrobromic acid (HBr)	48	1.49	9N
5. Hydroiodic acid (HI)	57	1.70	7N
6. Nitric acid (HNO_3)	70	1.42	16N
7. Sulfuric acid (H_2SO_4)	96	1.84	36N
8. Phosphoric acid (H_3PO_4)	85	1.69	45N
9. Perchloric acid (HClO_4)	60	1.54	9N

Aqua-Regia: Immediately before use, mix 3 volume of concentrated hydrochloric acid with 1 volume of concentrated nitric acid. The solution does not keep well. Perform all operations with aqua-regia under **FUME CUPBOARD**.

Chromosulfuric acid (Chromic acid): Dissolve 10 g of potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) or sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) in minimum volume of water in a beaker. Add ~100 ml of concentrated sulfuric acid carefully while stirring with a glass rod. Cool to room temperature. Preserve the dark brown solution in a clean well stoppered glass bottle. The solution has strong oxidizing and dehydrating properties. It should be handled with **great caution** (preferably using eye glasses and hand gloves). It is a very good cleansing agent for glass apparatus. For best result, the mixture should be left over night in the glass vessels to be cleaned. So long the colour is brown, the used portion may be poured back into the original stock. As brownish colour slowly changes to green, the mixture should be poured into a large volume of water and discarded. Ammonium dichromate, $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, should not be treated with conc. H_2SO_4 as it may explode due to heat of reaction.



Appendix-B2

Strengths of Diluted Acid Solutions

Sl. No.	Acids	Approximate Normality (N)	g.lit^{-1} (or ml.lit^{-1})
1.	Acetic Acid	5N 2N	Dilute 285 ml of glacial acetic acid to 1 litre with water 115 ml/litre
2.	Hydrochloric acid	5N 2N	Dilute 430 ml of conc.HCl to 1 litre with water, 175 ml/litre
3.	Sulfuric acid	5N 2N	Pour ~140 ml of conc. H_2SO_4 slowly with constant stirring into 500 ml of water in a beaker, cool to room temperature and dilute to 1 litre with water. 56 ml/litre
4.	Nitric acid	5N 2N	Dilute 310 ml of conc. HNO_3 to 1 litre with water. 125 ml /litre.
5.	Sulfurous acid (SO_2 -water)	~0.3N (~6-7% by weight)	Saturated solution of $\text{SO}_2(\text{g})$ in water.

Appendix-B3

Strengths of Dilute Solutions of Bases (Alkalies)

Sl. No.	Bases	Approximate Normality (N)	g.lit^{-1} (or ml.lit^{-1})
1.	Concentrated ammonia solution	15N (sp. gr. 0.88, 28% by wt.)	Commercial product may be used directly.
2.	Dilute ammonia solution	5N 2N	Dilute 335 ml of conc. NH_3 to 1 litre with water. ~135 ml/litre.
3.	Sodium hydroxide (caustic soda) solution	5N 2N	Dissolve ~220 g of pure NaOH(~90%) in water and dilute to 1 litre. 88 g/litre.
4.	Potassium hydroxide (caustic potash) solution	2N	Dissolve ~125 g of pure KOH (~90%) in water and dilute to 1 litre.

Appendix-B3 (Continued)

Sl. No.	Bases	Approximate Normality (N)	<i>g.lit.⁻¹ (or ml.lit.⁻¹)</i>
5.	Calcium hydroxide solution (lime-water)	0.04N	Shake ~2-3 g of calcium hydroxide with ~1 litre of water, allow to stand for a few minutes and syphon off or filter the liquid, which is a saturated solution of calcium hydroxide. Preserve in a corked (rubber cork) bottle, protecting from air (CO ₂).
6.	Barium hydroxide solution (baryta-water)	0.4N	Shake ~70 g of crystallized barium hydroxide (baryta), Ba(OH) ₂ .8H ₂ O, with ~1 litre of water. Allow to stand for a few minutes. Syphon off or filter the liquid, preserve in a corked (rubber cork) bottle, protecting from air (CO ₂).

Appendix-B4

Common Acid-Base Indicator Solutions

Sl. No.	Indicator (pH-range)	Concentration	Procedure (Colour : Acid → Base)
1.	Methyl orange (3.1-4.4)	0.1%	0.1g of methyl orange in 100ml of water. (orange-red → yellow).
2.	Methyl red (4.2-6.2)	0.1%	Dissolve 0.1g of methyl red in 100ml of 60% (v/v) ethanol. (red → yellow).
3.	Bromothymol blue (6.0-7.6)	0.05%	Dissolve 0.05g of bromothymol blue in 100 ml of 20% (v/v) ethanol. (yellow to blue).
4.	Phenol red (6.8-8.4)	0.1%	Dissolve 0.1g of phenol red in 100 ml of 20% (v/v) ethanol. (yellow → red).
5.	Phenolphthalin (8.2-10.0)	0.1%	Dissolve 0.1g of phenolphthalin [C ₆ H ₄ (COOH)CH(C ₆ H ₄ OH) ₂], in 100ml of 60% (v/v) ethanol. (colourless → purple).
6.	Bromocresol green (3.8-5.4)	0.1%	Dissolve 0.1g of bromocresol green in 100 ml of 20% (v/v) ethanol. (yellow → blue).
7.	Mixed Indicator Methyl red & Methylene blue (4.6)	0.2% 0.1%	0.2g of methyl red and 0.1g of methylene blue in 100 ml of 96% ethanol. (red-violet → green)



Appendix-B5

Solid Reagents

Trivial Name	Chemical Formula
A Aluminium (foil, powder)	Al
Aluminium alum	$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
Aluminium oxide	Al_2O_3
Aluminium phosphate	$AlPO_4$
Aluminium sulfate	$Al_2(SO_4)_3 \cdot 18H_2O$
Ammonium acetate	CH_3COONH_4
Ammonium bifluoride	NH_4HF_2
Ammonium bromide	NH_4Br
Ammonium carbonate	$(NH_4)_2CO_3$
Ammonium chloride	NH_4Cl
Ammonium dichromate	$(NH_4)_2Cr_2O_7$
Ammonium dihydrogenphosphate	$NH_4H_2PO_4$
Ammonium fluoride	NH_4F
Ammonium molybdate	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$
Ammonium nitrate	NH_4NO_3
Ammonium oxalate	$(NH_4)_2C_2O_4 \cdot H_2O$
Ammonium peroxodisulfate	$(NH_4)_2S_2O_8$
Ammonium sodium hydrogenphosphate (Microcosmic salt)	$NH_4NaHPO_4 \cdot 4H_2O$
Ammonium sulfate	$(NH_4)_2SO_4$
Ammonium thiocyanate	NH_4SCN
Antimony (III) oxide	Sb_2O_3
Antimony (III) sulfide	Sb_2S_3
Antimony (V) sulphide	Sb_2S_5
Arsenic (III) oxide (Poison)	As_2O_3
Arsenic (III) sulfide (Poison)	As_2S_3
Asbestos (pulp, fibre)	
B Barium carbonate	$BaCO_3$
Barium chloride	$BaCl_2 \cdot 2H_2O$
Barium chromate	$BaCrO_4$

Appendix-B5 (Continued)

Barium hydroxide	$\text{Ba(OH)}_2 \cdot 8\text{H}_2\text{O}$
Barium nitrate	$\text{Ba(NO}_3)_2$
Barium nitrite	$\text{Ba(NO}_2)_2 \cdot 4\text{H}_2\text{O}$
Barium oxide	BaO
Barium sulfate	BaSO_4
Barium sulfide	BaS
Barium thiosulfate	BaS_2O_3
Bismuth oxychloride	BiOCl
Bismuth oxynitrate	$\text{BiO(NO}_3)$
Bismuth nitrate	$\text{Bi(NO}_3)_3 \cdot 5\text{H}_2\text{O}$
Bismuth phosphate	BiPO_4
Bismuth sulfide	Bi_2S_3
Borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Boric acid	H_3BO_3

C. Cadmium carbonate	CdCO_3
Cadmium chloride	$\text{CdCl}_2 \cdot x\text{H}_2\text{O}$ ($x=1, 2\frac{1}{2}$)
Cadmium iodide	CdI_2
Cadmium phosphate	$\text{Cd}_3(\text{PO}_4)_2$
Cadmium sulfate	$\text{CdSO}_4 \cdot (8/3)\text{H}_2\text{O}$
Cadmium sulfide	CdS
Calcium (metal powder)	Ca
Calcium carbonate	CaCO_3
Calcium chloride (anhydrous)	CaCl_2
Calcium chromate	CaCrO_4
Calcium fluoride	CaF_2
Calcium hydroxide	Ca(OH)_2
Calcium hydrogenphosphate	CaHPO_4
Calcium iodate	$\text{Ca(IO}_3)_2$
Calcium nitrite	$\text{Ca(NO}_2)_2 \cdot 4\text{H}_2\text{O}$
Calcium phosphate	$\text{Ca}_3(\text{PO}_4)_2$
Calcium sulfate	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
Calcium sulfite	$\text{CaSO}_3 \cdot 2\text{H}_2\text{O}$

Appendix-B5 (Continued)

Chrome alum	$K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$
Chromic acid	CrO_3
Chromic oxide	Cr_2O_3
Chromium phosphate	$CrPO_4$
Cobalt carbonate	$CoCO_3$
Cobalt oxide	CoO
Cobalt sulfate	$CoSO_4$
Cobalt sulfide	CoS
Copper (turnings, Cu-T)	Cu
Copper (II) arsenate	$Cu_3(AsO_4)_2$
Copper (II) chloride	$CuCl_2 \cdot 2H_2O$
Copper (II) nitrate	$Cu(NO_3)_2 \cdot 6H_2O$
Copper (II) oxide	CuO
Copper (II) sulfate	$CuSO_4 \cdot 5H_2O$
Copper (II) sulfide	CuS
D. Davarda's alloy	$Cu (50\%), Al (45\%), Zn (5\%)$
Disodium hydrogenphosphate	$Na_2HPO_4 \cdot 2H_2O$
E. Ethyl potassium xanthate	$C_2H_5O(C=S)SK$
F. Fusion mixture	$Na_2CO_3 + K_2CO_3 (1:1)$
G. Glass wool	
H. Hydrazine sulfate	$N_2H_4 \cdot H_2SO_4$
Hydroquinone (quinol)	$p-C_6H_4(OH)_2$
Hydroxylamine hydrochloride	$NH_2OH \cdot HCl$
I. Iron (fillings, nails, wire)	Fe
Iron (II) ammonium sulfate (Mohr's salt)	$(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$
Iron (II) sulfate (Ferrous sulfate)	$FeSO_4 \cdot 7H_2O$
Iron (III) ammonium sulfate (Ferric alum)	$(NH_4)_2SO_4 \cdot Fe_2(SO_4)_3 \cdot 24H_2O$
Iron (III) chloride (Ferric chloride)	$FeCl_3 \cdot xH_2O (x = 2, 6)$
Iron (III) nitrate (Ferric nitrate)	$Fe(NO_3)_3 \cdot 6H_2O$
Iron (III) oxide (Ferric oxide)	Fe_2O_3
Iron (III) phosphate (Ferric phosphate)	$FePO_4$

Appendix-B5 (Continued)

L	Lead (crucible with lid)	Pb
	Lead arsenate	$\text{Pb}_3(\text{AsO}_4)_2$
	Lead acetate (solution, paper)	$(\text{CH}_3\text{COO})_2\text{Pb} \cdot 2\text{H}_2\text{O}$
	Lead bromide	PbBr_2
	Lead carbonate	PbCO_3
	Lead chloride	PbCl_2
	Lead chromate	PbCrO_4
	Lead iodide	PbI_2
	Lead nitrate	$\text{Pb}(\text{NO}_3)_2$
	Lead oxide; (Red lead); lead dioxide	PbO ; (Pb_3O_4) ; PbO_2
	Lead phosphate	$\text{Pb}_3(\text{PO}_4)_2$
	Lead sulfate	PbSO_4
	Lead sulfide	PbS
	Litmus (test) paper (red & blue)	
M	Magnesium metal (powder, turnings)	Mg
	Magnesium carbonate	MgCO_3
	Magnesium chloride	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$
	Magnesium nitrate	$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
	Magnesium oxide	MgO
	Magnesium phosphate	$\text{Mg}_3(\text{PO}_4)_2$
	Manganese dioxide	MnO_2
	Manganese (II) sulfate	$\text{MnSO}_4 \cdot x\text{H}_2\text{O}$ ($x = 1, 4, 5, 7$)
	Manganese (II) metaborate	$\text{Mn}(\text{BO}_2)_2$
	Mercury (I) chloride (calomel)	Hg_2Cl_2
	Mercury (II) chloride	HgCl_2
	Mercury (II) nitrate (solution, paper)	$(\text{H}^+)_2[\text{Hg}(\text{NO}_3)_4]^{2-}$
	Mercury (II) iodide	HgI_2
	Mercury (II) oxide	HgO (yellow)
	Mercury (II) sulfide	HgS (yellow & black)
	Microcosmic salt	cf. ammonium sodium hydrogenphosphate
	Mohr's salt	cf. iron(II) ammonium sulfate
N.	Nickel metal (crucible, lid, foil, spatula)	Ni
	Nickel carbonate	NiCO_3

Appendix-B5 (Continued)

Nickel oxide	NiO
Nickel sulfate	$\text{NiSO}_4 \cdot x\text{H}_2\text{O}$ ($x=6, 7$)
Nickel sulfide	NiS
O Oxalic acid	$\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
P Phenol (carbolic acid)	$\text{C}_6\text{H}_5\text{OH}$
Platinum metal (foil, crucible, wire, spatula)	Pt
Potassium antimonytartarate	$\text{K}(\text{Sb}=\text{O})\text{C}_4\text{H}_4\text{O}_6 \cdot (\frac{1}{2})\text{H}_2\text{O}$
Potassium bromate	KBrO_3
Potassium bromide	KBr
Potassium carbonate	$\text{K}_2\text{CO}_3 \cdot (1\frac{1}{2})\text{H}_2\text{O}$
Potassium chloride	KCl
Potassium chromate	K_2CrO_4
Potassium cyanide (<i>Poison</i>)	KCN
Potassium dichromate (<i>crystals</i>)	$\text{K}_2\text{Cr}_2\text{O}_7$
Potassium dihydrogenphosphate	KH_2PO_4
Potassium ferricyanide	$\text{K}_3[\text{Fe}(\text{CN})_6]$
Potassium ferrocyanide	$\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$
Potassium fluoride	KF
Potassium hydrogenfluoride	$\text{KHF}_2 \cdot x\text{H}_2\text{O}$ ($x = 2, 4$)
Potassium hydrogensulfate	KHSO_4
Potassium hydrogentartarate	$\text{KHC}_4\text{H}_4\text{O}_6$
Potassium hydroxide	$\text{KOH} \cdot x\text{H}_2\text{O}$ ($x = 1, 2, 4$)
Potassium iodate	KIO_3
Potassium iodide	KI
Potassium nitrate	KNO_3
Potassium nitrite	KNO_2
Potassium periodate	KIO_4
Potassium permanganate	KMnO_4
Potassium peroxodisulfate	$\text{K}_2\text{S}_2\text{O}_8$
Potassium-sodium tartarate (Rochelle salt, or, Seignet salt)	$\text{KOOC-CH}(\text{OH})\text{CH}(\text{OH}).\text{COONa} \cdot 4\text{H}_2\text{O}$
Potassium thiocyanate	KSCN
R. Resorcinol	1,3 - $\text{C}_6\text{H}_4(\text{OH})_2$

Appendix-B5 (Continued)

S. Salicylic acid	$1,2\text{-C}_6\text{H}_4(\text{COOH})(\text{OH})$
Sulfosalicylic acid	$1,2,5\text{-C}_6\text{H}_3(\text{COOH})(\text{OH})(\text{SO}_3\text{H})$
Silica	SiO_2
Silicic acid	$\text{SiO}_2 \cdot x\text{H}_2\text{O}$
Silver metal (wire, foil, spatula)	Ag
Silver chloride	AgCl
Silver chromate	Ag_2CrO_4
Silver nitrate	AgNO_3
Silver sulfate	Ag_2SO_4
Sodalime	$\text{NaO} \cdot \text{CaO} (\sim 1:4)$
Sodium metal (Caution)	Na
Sodium acetate	$\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$
Sodium arsenate	Na_3AsO_4
Sodium arsenite	NaAsO_2
Sodium azide	NaN_3
Sodium bismuthate	NaBiO_3
Sodium bromide	NaBr
Sodium carbonate (anhydrous)	Na_2CO_3
Sodium chloride	NaCl
Sodium cobaltinitrite	$\text{Na}_3[\text{Co}(\text{NO}_2)_6]$
Sodium dithionite	$\text{Na}_2\text{S}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
Sodium fluoride	NaF
Sodium formate	HCOONa
Sodium hydrogencarbonate	NaHCO_3
Sodium hydroxide	NaOH
Sodium hypophosphite	NaH_2PO_2
Sodium nitrate	NaNO_3
sodium nitrite	NaNO_2
Sodium nitroprusside	$\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$
Sodium oxalate (Sorensen's salt)	$\text{Na}_2\text{C}_2\text{O}_4$
Sodium perchlorate	NaClO_4
Sodium peroxide (Explosive)	Na_2O_2
Sodium peroxoborate	$\text{NaBO}_3 \cdot 4\text{H}_2\text{O}$

Appendix-B5 (Continued)

Sodium phosphite	$\text{Na}_2\text{HPO}_3 \cdot 5\text{H}_2\text{O}$
Sodium sulfate (anhydrous)	Na_2SO_4
Sodium sulfite (anhydrous)	Na_2SO_3
Sodium tetraborate (borax)	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
Sodium thiosulfate	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$
Starch	$(\text{C}_6\text{H}_{10}\text{O}_5)_n$
Sulfamic acid	$\text{H}_2\text{N} \cdot \text{SO}_3\text{H}$
Sulfur (powder)	S
Strontium carbonate	SrCO_3
Strontium nitrate	$\text{Sr}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
Strontium chromate	SrCrO_4
Strontium sulfate	SrSO_4
Strontium phosphate	$\text{Sr}_3(\text{PO}_4)_2$
Strontium molybdate	SrMoO_4
T. Tartaric acid	$\text{HOOC} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$
Tin (granulated, globules)	Sn
Tin (II) chloride (stannous chloride)	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
Tin (II) sulfide	SnS
Tin dioxide	SnO_2
Thiourea	$\text{S}=\text{C}(\text{NH}_2)_2$
Turmeric paper	
U. Uranyl acetate	$\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$
Uranyl nitrate	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Urea	$\text{O}=\text{C}(\text{NH}_2)_2$
Z. Zinc (dust, granulated)	Zn
Zinc acetate	$(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$
Zinc borate	$\text{Zn}(\text{BO}_2)_2$
Zinc carbonate	ZnCO_3
Zinc nitrate	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Zinc oxide	ZnO
Zinc phosphate	$\text{Zn}_3(\text{PO}_4)_2$
Zinc sulfate	$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$
Zinc sulfide	ZnS

Appendix-B5 (Continued)

Compounds of Rare Elements

Trivial name	Chemical formula
Be Beryllium hydroxide	$\text{Be}(\text{OH})_2$
Beryllium nitrate	$\text{Be}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$
Beryllium oxide	BeO
Beryllium sulfate	$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$
Ce Ceric ammonium nitrate	$(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$
Ceric oxide	$\text{CeO}_2 \cdot x\text{H}_2\text{O}$
Ceric ammonium sulfate	$\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$
Ceric sulfate	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
Mo Ammonium molybdate	$(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$
Molybdic acid	$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$
Phosphomolybdic acid	$\text{H}_3[\text{PMo}_{12}\text{O}_{40}]$
Molybdenum disulfide	MoS_2
Sodium molybdate	Na_2MoO_4
Th Thorium dioxide	$\text{ThO}_2 \cdot x\text{H}_2\text{O}$
Thorium nitrate	$\text{Th}(\text{NO}_3)_4 \cdot x\text{H}_2\text{O}$ ($x = 4, 5$)
Thorium sulfate	$\text{Th}(\text{SO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x = 4, 6, 8, 9$)
Potassium thorium sulfate	$\text{K}_4[\text{Th}(\text{SO}_4)_4]$
Thorium iodate	$\text{Th}(\text{IO}_3)_4$
Ti Titanium dioxide	TiO_2
Titanium hydrogenphosphate	$\text{Ti}(\text{HPO}_4)_2$
Potassium titanium fluoride	K_2TiF_6
Titanium sulfate	$\text{TiOSO}_4 \cdot \text{H}_2\text{O}$
U. Ammonium diuranate	$(\text{NH}_4)_2\text{U}_2\text{O}_7$
Uranyl ammonium phosphate	$\text{UO}_2(\text{NH}_4)\text{PO}_4$
Uranyl hydrogenphosphate	UO_2HPO_4
Uranyl carbonate	UO_2CO_3
Uranium oxides	$\text{UO}_2, \text{U}_3\text{O}_8$
Uranyl nitrate	$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

Appendix-B5 (Continued)

V. Ammonium vanadate	NH_4VO_3
Vanadium pentoxide	V_2O_5
Vanadyl sulfate	$\text{VOSO}_4 \cdot x\text{H}_2\text{O}$ ($x = 2, 5$)
Sodium vanadate	NaVO_3
W. Tungstic acid	$\text{WO}_3 \cdot 2\text{H}_2\text{O}$
Sodium tungstate	$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$
Phosphotungstic acid	$\text{H}_3[\text{PO}_4(\text{W}_{12}\text{O}_{36})]$
Zr. Zirconium dioxide	$\text{ZrO}_2 \cdot x\text{H}_2\text{O}$
Zirconium fluoride	$\text{ZrF}_4 \cdot x\text{H}_2\text{O}$ ($x = 1, 3$)
Zirconyl chloride	$\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$
Zirconyl nitrate	$\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$
Zirconium hydrogen phosphate	$\text{Zr}(\text{HPO}_4)_2 \cdot x\text{H}_2\text{O}$ ($x = 1, 2$)
Zirconium sulfate	$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$
Ammonium zirconium sulfate	$(\text{NH}_4)_2[\text{Zr}(\text{SO}_4)_3] \cdot 3\text{H}_2\text{O}$

Appendix-B6

Organic Liquids and Solvents

Organic liquids	B.P(°C) [density.g.cm ⁻³]	Physical nature
1. Acetone CH_3COCH_3	56.2 [0.79]	Clear colourless volatile liquid with characteristic odour.
2. Acetylacetone $\text{CH}_3\text{CO} \cdot \text{CH}_2\text{CO} \cdot \text{CH}_3$	137 [0.97]	Colourless liquid, commercial product is slightly yellow.
3. <i>iso</i> -Amyl alcohol [#] $(\text{CH}_3)_2\text{CHCH}_2\text{CH}_2\text{OH}$	132 [0.813]	Colourless liquid with pungent odour. CAUTION: Handle carefully. Preserve in closed metal box under a cupboard provided with exhaust.
4. <i>iso</i> -Amylacetate [#] $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	142 [0.876]	Colourless liquid with pleasant odour.
5. Aniline $\text{C}_6\text{H}_5\text{NH}_2$	184-186 [1.02]	Colourless oily liquid with characteristic odour. Darkenes slowly on exposure to air. Preserve in dark coloured bottle.

Appendix-B6 (Continued)

Organic liquids	B.P(°C) [density.g.cm ⁻³]	Physical nature
6. Benzene (C ₆ H ₆) [#]	81.1 [0.8787]	Clear, colourless, highly inflammable liquid with characteristic odour. CAUTION: Don't inhale.
7. Carbon tetrachloride (CCl ₄) [#]	76.7 [1.589]	Colourless, clear, non inflammable heavy liquid with characteristic odour.
8. Chloroform (CHCl ₃) [#] (Anesthetic)	61-62 [1.484]	Colourless, sweet smelling liquid. CAUTION: Don't inhale chloroform vapour. Preserve in a metal box under a cupbrard provided with exhaust.
9. Ethanol (anhydrous) [#] Absolute alcohol C ₂ H ₅ OH	78.5 [0.798]	Commercial product (~99.7% C ₂ H ₅ OH). Sold under permit. CAUTION: Inflammable, preserve in metal box or under cupboard.
10. Ethanol (96%) Ethyl alcohol	[0.81]	Commercial product (~95-96% C ₂ H ₅ OH) Sold under permit. CAUTION: Inflammable. Preserve in metal box or under a cupboard.
11. Ethanol (80%) Rectified spirit		80 ml of 96% ethanol and 16 ml of water. Sold under permit. CAUTION: Inflammable. Preserve in metal box or under a cupboard.
12. Ethylacetate CH ₃ COOC ₂ H ₅	77 [0.902]	Colourless pleasant smelling liquid.
13. Ethylamine [#] CH ₃ CH ₂ NH ₂	16.6 [0.689] 1M	Flamable liquid, ammonia odour, strongly alkaline reaction. Dissolve 4.5g of ethylanine in 100 ml of water, or, dilute 1 ml of 70% ethylamine with water upto 100 ml.
14. Ethylenediamine [#] H ₂ NCH ₂ CH ₂ NH ₂	116-117 [0.898]	Colourless, thick, volalite liquid with characteristic ammonia odour. Forms white fumes in contact with moist air, gradually turns sticky brown liquid on exposure to air.

Appendix-B6 (Continued)

Organic liquids	B.P(°C) [density.g.cm ⁻³]	Physical nature
15. Formaldehyde solution (40% HCHO), Formalin	96 [1.08]	Commercial product is 40% HCHO, i.e., 40 g of HCHO per 100 ml of solution. It has a characteristic pungent odour. It contains some methanol as stabilizer. White solid, paraldehyde, precipitates on long standing.
16. Formaldehyde solution (10% HCHO)		Mix 10 ml of 40% formaldehyde solution (formalin) with 30 ml of water.
17. Glycerol CH ₂ (OH)CH(OH)CH ₂ (OH)	290 [1.262]	Syrupy liquid, sweet warm taste.
18. Mannitol	10%	Dissolve 10 g of mannitol, C ₆ H ₁₄ O ₆ in water, neutralize with 0.01M sodium hydroxide solution using bromothymol blue indicator up to a just green end point, dilute to 100 ml with water.
19. Methanol (Methyl alcohol) CH ₃ OH	64.7 [0.79]	Colourless inflammable liquid with characteristic odour. CAUTION: Deadly poisonous , should never be tested nor inhaled or exposed to. Inflammable. Preserve in a metal box or in a cupboard.
20. Pyridine [#]	115-116 [0.98]	Clear colourless flammable liquid in pure state, having characteristic disagreeable odour. CAUTION: Should never be inhaled or touched or exposed to. Preserve in a sealed dark coloured bottle in a refrigerator.



Appendix-B7

Solutions of Salts of Some Common Cation and Anion Radicals

Salts [F.W.]	Approximate strength	Procedure
1. Aluminium sulfate $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ [630]	0.17M	10.7 g of $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ dissolved in 100 ml of water, or, 16 g of $\text{Al}_2(\text{SO}_4)_3 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$ dissolved in 100 ml of water. Add 3-4 drops of H_2SO_4 .
2. Ammonium acetate: $\text{NH}_4\text{COOCCH}_3$ [77]	3M	231g of the salt dissolved in 1 litre of water.
3. Ammonium carbonate: $(\text{NH}_4)_2\text{CO}_3$: The commercial salt is a 1:1 mixture of ammonium bicarbonate (NH_4HCO_3) and ammonium carbamate $\text{NH}_4\text{COONH}_2$.	4M	Dissolve ~160 g of the salt in a mixture of 140 ml of concentrated ammonia and 860 ml of water.
4. Ammonium chloride: NH_4Cl [53.5]	5M	~270 g of the salt dissolved in 1 litre of water.
5. Ammonium nitrate: NH_4NO_3 [80]	1M	80 g of the salt dissolved in 1 litre of water.
6. Ammonium oxalate: $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ [142]	0.25M	35 g of the salt dissolved in 1 litre of water.
7. Ammonium sulfate $(\text{NH}_4)_2\text{SO}_4$ [132]	1M	132 g of the salt dissolved in 1 litre of water.
8. Ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (ammonium paramolybdate): [1235.8]	0.25M	<i>Method - 1:</i> Dissolve 45 g of the commercial salt or 40 g of pure molybdic acid, MoO_3 , in a mixture of 70 ml of concentrated ammonia solution and 140 ml of water. When the dissolution is complete, add this solution slowly with vigorous stirring to a mixture of 250 ml of concentrated HNO_3 and 500 ml of water. Dilute to 1 litre, allow to stand overnight, collect the clear solution by decantation.

Appendix-B7 (Continued)

Salts [F.W.]	Approximate strength	Procedure
Note: (1) The alkaline solution of ammonium molybdate (<i>method-2</i>) keeps better than the acidic solution (<i>method-1</i>) (2) Before using the alkaline solution of ammonium molybdate, it has to be made slightly acidic with HNO_3. (3) Acid solution of ammonium molybdate has a tendency to separate solid (possibly) MoO_3, such tendency is much less with the alkaline solution.		
9. Colourless ammonium sulfide solution (actually NH_4HS solution)	1M	<i>Method - 2</i> : Dissolve 45g of the commercial salt in a mixture of 40 ml of concentrated ammonia and 60 ml of water. Add 120 g of ammonium nitrate, stir to dissolve the salt and dilute the mixture to 1 litre with water. Pass H_2S gas (Fume Chamber) into 200 ml of ice cold conc. NH_3 solution until saturation. (1 ml of the solution should not form any precipitate with 1M magnesium sulfate solution. Add a equal volume of concentrated ammonia and dilute to 1 litre. Keep the solution in well corked brown bottles in the cold, away from direct light.
10. Ammonium polysulfide, or yellow ammonium sulfide : $(\text{NH}_4)_2\text{S}_x$ Note: Commercially available solution may also be used.	1M	Pass H_2S (Fume Chamber) into 150 ml of ice cold concentrated ammonia solution until saturation. Add 10 g of finely powdered flower of sulfur and 250 ml of concentrated ammonia solution. Stir the mixture until the sulfur is dissolved, dilute to 1 litre with water. Store in a dark coloured well corked bottle in a cool place away from light.
11. (a) Ammonium thiocyanate : NH_4SCN [76]	0.1M	7.6 g of NH_4SCN dissolved in 1 litre of water.

Appendix-B7 (Continued)

Salts [F.W.]	Approximate strength	Procedure
(b) Ammonium thiocyanate: NH_4SCN [76]	saturated (in acetone)	Shake 1 g of NH_4SCN with 5 ml of acetone. Use the clear supernatant liquid for the test.
	0.5M	38 g of the salt dissolved in 1 litre of water.
12. Barium chloride: $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ [244.34]	0.25M	Dissolve 61 g of the salt in water and dilute to 1 litre.
13. Barium nitrate: $\text{Ba}(\text{NO}_3)_2$ [261.34]	0.25M	Dissolve 65 g of the salt in water and dilute to 1 litre.
14. Bismuth nitrate	0.2M	Dissolve 9.7 g of bismuth nitrate pentahydrate, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in a mixture of 50 ml of water and 5 ml of concentrated nitric acid. Dilute the mixture to 100 ml with water.
15. Cadmium sulfate $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$	0.25M	Dissolve 6.4 g of trisulfate octahydrate in 100 ml of water.
16. Calcium chloride: $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ [219]	0.25M	Dissolve 55 g of the salt in water and dilute to 1 litre.
17. Calcium sulfate : $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ [172]	0.015M (saturated)	Shake ~3g of the salt with 1 litre of water for a long time. Allow to stand. Filter or syphon off the saturated solution after several hours.
18. Cobalt nitrate: $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [290.93]	0.15M	Dissolve 44 g of the salt in water and dilute to 1 litre.
19. Copper (I) chloride reagent*	1M	Dissolve 9.9 of copper (I) chloride, CuCl , in a mixture of 40 ml of conc. HCl and 60 ml of water by heating. Add a few strips of metallic copper to the solution.
20. Copper sulfate: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ [249.54]	0.5M	Dissolve 125 g of the salt in 1 litre of water containing 3 ml of concentrated sulfuric acid.
21. Chromium (III) chloride $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ [266.5]	0.33M	Dissolve 8.8g of the salt in 100 ml of 1 M HCl solution.

Appendix-B7 (Continued)

Salts [F.W.]	Approximate strength	Procedure
22. Disodium hydrogen phosphate	0.033M	Dissolve either disodium hydrogen orthophosphate (anhydrous) : Na_2HPO_4 (4.2g), or, dihydrate: $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (6 g), or dodecahydrate : $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ (12 g) in water and dilute to 1 litre.
23. Disodium hydrogen arsenate [POISON]	0.25M	Dissolve 7.6 g of disodium hydrogen arsenate heptahydrate, $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ in water and dilute to 100 ml.
	0.1 M	3.04 g of the salt dissolved in 100 ml of water.
24. Ferric chloride $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ [270]	0.5M	Dissolve 135g of the salt in 1 litre of water containing 20 ml of concentrated hydrochloric acid.
25. Ferrous sulfate $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ [277]	0.5M	Dissolve ~140 g of the salt in 1 litre of water containing 7 ml of concentrated sulfuric acid.
26. Lead acetate $\text{Pb}(\text{OOCCH}_3)_2 \cdot 3\text{H}_2\text{O}$ [379]	0.25M	Dissolve 95 g of the salt in 1 litre of water containing 10 ml of glacial acetic acid.
27. Lead nitrate $\text{Pb}(\text{NO}_3)_2$ [331.23]	0.25M	Dissolve ~83g of the salt in 1 litre of water adding 2-3 drops of concentrated nitric acid.
28. Magnesium sulfate $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ [246]	0.25M	Dissolve 62 g of the salt in 1 litre of water.
29. Magnesia mixture $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ [203] + NH_4Cl [53.5]	0.5M (Mg^{2+}) 2M (NH_4^+) 0.75M (NH_3)	Dissolve 100 g of magnesium chloride and 100 g of ammonium chloride in water, add 50 ml of concentrated ammonia and dilute to 1 litre with water.
30. Magnesium nitrate reagent: $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [256] (ammoniacal)	0.5M (Mg^{2+}) 3M (NH_4^+) 0.25M (NH_3)	Dissolve ~130 g of the salt and 240 g of ammonium nitrate in water, add 15-20 ml of concentrated ammonia and dilute to 1 litre.

Appendix-B7 (Continued)

Salts [F.W.]	Approximate strength	Procedure
31. Manganous chloride reagent: $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ [197.94]	Saturated	Take ~100 ml of concentrated hydrochloric acid, add powdered manganous chloride and stir until the solution is saturated (i.e., no further amount of the salt dissolves).
32. Manganous sulfate $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ [222.94]	Saturated	Shake ~4g of $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$ with 6 ml of water. Allow to stand for 24 hours. Use the clear supernatant liquid for the tests.
33. Mercury (I) chloride (calomel) suspension* [POISON]	Saturated	Add 1 ml of 2M hydrochloric acid to 5 ml of 0.05 M mercury (I) nitrate. Wash the precipitate 4-5 times with water by centrifugation. Suspend the precipitate in ~5 ml of water. Preserve in a well corked bottle.
34. Mercury (II) chloride [POISON]	Saturated	Shake 7 g of mercury (II) chloride HgCl_2 , with 100 ml of water, allow to stand for 24 hours. Use the clear supernatant liquid for the tests.
	0.05M	Dissolve ~1.4 g of HgCl_2 in water and dilute to 100 ml.
	5% (in alcohol)	Dissolve 1 g of HgCl_2 in 20 ml of 96% ethanol.
35. Mercury (I) nitrate [POISON]	0.05M	Dissolve 2.81 g of mercury (I) nitrate dihydrate, $\text{Hg}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, in a cold mixture of 50 ml of water and 1 ml of concentrated nitric acid. Dilute the solution to 100 ml with water.
36. Nickel (II) chloride	0.5M	Dissolve 11.9 g of nickel (II) chloride hexahydrate, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, in 100 ml of water.
37. Nickel (II) sulfate	0.5M	Dissolve 14 g of nickel (II) sulfate heptahydrate, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in water and dilute to 100 ml.
38. Potassium antimonate	0.2M	Dissolve 5 g of potassium antimonate, $\text{K}[\text{Sb}(\text{OH})_6]$, in water and dilute to 100 ml.

Appendix-B7 (Continued)

Salts [F.W.]	Approximate strength	Procedure
39. Potassium bromate	0.1M	Dissolve 1.67 g of potassium bromate, KBrO_3 in 100 ml of water.
40. Potassium bromide	0.1M	Dissolve 1.19 g of potassium bromide, KBr , in 100 ml of water.
41. Potassium chloride	1M	Dissolve 7.46 g of potassium chloride in 100 ml of water.
42. Potassium chromate K_2CrO_4 [194]	0.25M	Dissolve 49-50 g of the salt in 1 litre of water.
43. Potassium cyanide KCN [65]	0.5M	[Poison] . Dissolve ~3-3.5 g of the salt in 100 ml of water.
44. Potassium dichromate $\text{K}_2\text{Cr}_2\text{O}_7$ [294]	0.1N	Dissolve ~5 g of the salt in 1 litre of water.
45. Potassium ferricyanide $\text{K}_3[\text{Fe}(\text{CN})_6]$, [328.85]	0.033M	Dissolve 10.98 g (~11 g) of potassium ferricyanide, $\text{K}_3[\text{Fe}(\text{CN})_6]$ in water and dilute to 1 litre.
46. Potassium ferrocyanide $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ [421.85]	0.025M	Dissolve 10.5 g of potassium ferrocyanide trihydrate, $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ in water and dilute to 1 litre.
47. Potassium iodide KI , [166]	0.5M	Dissolve 83 g of the salt in 1 litre of water.
48. Potassium iodate	0.1M	Dissolve 2.14 g of potassium iodate, KIO_3 in 50 ml of hot water, cool and dilute to 100 ml with water.
49. Potassium nitrate	0.1M	Dissolve 10.1g of potassium nitrate, KNO_3 , in 1 litre of water.
50. Potassium nitrite	0.1M	Dissolve 0.9 g of potassium nitrite, KNO_2 , in water and dilute to 100 ml.
51. Potassium permanganate KMnO_4 [157.94]	0.1N	Dissolve ~3.2 g of the salt in 1 litre of water. Allow to stand over night. Filter through glass wool. Preserve in dark coloured bottle away from light.
52. Potassium-sodium tartarate	0.1M	Dissolve 28.2 g of potassium sodium tartarate tetrahydrate, $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$ (Rochelle salt or Seignette salt) in water and dilute to 1 litre.

Appendix-B7 (Continued)

Salts [F.W.]	Approximate strength	Procedure
53. Potassium sulfate	Saturated	Shake 10 g of potassium sulfate, K_2SO_4 , with 90 ml of water. Allow to stand for 24 hours. Use the clear supernatant liquid for the tests.
54. Potassium thiocyanate KSCN [97]	0.5M	Dissolve 49 g of the salt in 1 litre of water.
55. Silver nitrate $AgNO_3$ [170]	0.1M	Dissolve 17 g of the salt in 1 litre of water.
56. Silver sulfate Ag_2SO_4 [312]	0.025 (M) (~saturated)	Dissolve 8 g of the salt in 1 litre of water.
57. Sodium acetate $Na(OOCCH_3) \cdot 3H_2O$ [136]	3M	Dissolve 408 g of the crystallized salt in 1 litre of water.
58. Sodium arsenite	0.1M	Dissolve 1.3 g of sodium metaarsenite, $NaAsO_2$, in water and dilute to 100 ml.
59. Sodium carbonate $Na_2CO_3 \cdot 10H_2O$ [286]	1.5M	Dissolve 430 g of the crystallized salt in 1 litre of water.
60. Sodium chloride [58.5]	0.1 M	Dissolve ~5.85g of sodium chloride, $NaCl$, in water and dilute to 1 litre.
61. Sodium cobaltinitrite $Na_3[Co(NO_2)_6]$ [403.93]	~0.15M	1.5 to 2g of the (AR) salt in 25 ml of water. Alternatively, dissolve ~0.7-0.8g of cobalt nitrate $Co(NO_3)_2 \cdot 6H_2O$ in ~5 ml of water, 6 g of sodium nitrite in ~5 ml of water and mix the two solutions with stirring. To the resulting mixture add 1.5 ml of glacial acetic acid and dilute to 25 ml. Allow to stand for some time and filter. The solution does not keep for more than 3-4 weeks.
62. Sodium dithionite S	0.5M	Dissolve 10.5 g of sodium dithionite dihydrate, $Na_2S_2O_4 \cdot 2H_2O$, in water and dilute to 100 ml. Note: Freshly prepared solution should be used.

Appendix-B7 (Continued)

Salts [F.W.]	Approximate strength	Procedure
63. Sodium hypochlorite NaOCl solution	~5-7% (w/v)	Dilute the commercial product with equal volume of water.
64. Sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$ [297.85]	...	Prepare the solution as and when required. Dissolve a small crystal of the salt in ~5 ml of water.
65. Sodium sulfide	2M	Dissolve 20 g of sodium hydroxide (NaOH) in 100 ml of water, divide the solution into two equal parts. Pass H_2S gas (Fume Cupboard) into one part until saturation ($\text{NaOH} + \text{H}_2\text{S} \rightarrow \text{NaHS} + \text{H}_2\text{O}$), and add this solution to the remaining part of the NaOH solution ($\text{NaOH} + \text{NaHS} \rightarrow \text{Na}_2\text{S} + \text{H}_2\text{O}$).
66. Sodium sulfite*	0.5M	Dissolve 6.3 g of sodium sulfite, Na_2SO_3 or 12.6 g of sodium sulfite heptahydrate, $\text{Na}_2\text{SO}_3\cdot 7\text{H}_2\text{O}$ in water and dilute to 100 ml.
67. Sodium sulfate	0.1M	Dissolve 3.22 g of sodium sulfate decahydrate, $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ in water and dilute to 100 ml.
68. Sodium silicate*	1M	Dilute 20 ml of commercial (30%) water glass solution to 100 ml with water.
69. Sodium thiosulfate	0.1M	Dissolve 24.8 g of sodium thiosulfate pentahydrate in water and dilute to 1 litre.
70. Strontium nitrate	0.25M	Dissolve 5.29 g of strontium nitrate in water and dilute to 100 ml.
71. Stannous chloride $\text{SnCl}_2\cdot 2\text{H}_2\text{O}$ [226]	0.25M	Dissolve ~56.5 g of the salt in 100 ml of hot concentrated hydrochloric acid and dilute to 1 litre. Keep a few small pieces of metallic tin in the bottle to prevent aerial oxidation of Sn^{II} to Sn^{IV} .
72. Zirconyl nitrate reagent (For fluoride test)		Dissolve ~0.1 g of zirconyl nitrate in 20 ml of concentrated hydrochloric acid and dilute to 100 ml with water.

Appendix-B7 (Continued)

Salts [F.W.]	Approximate strength	Procedure
73. Zirconyl nitrate (for phosphate separation)		Heat 10 g of commercially pure zirconyl nitrate, $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$, free from iron and 100 ml of 1 M HNO_3 (6.2 ml of conc. HNO_3 diluted to 100 ml) to boiling with constant stirring. Allow to stand for 24 hours. Decant or syphon off the clear solution.
74. Zinc acetate $\text{Zn}(\text{OOCCH}_3)_2 \cdot 2\text{H}_2\text{O}$	0.1M	Dissolve 2.19 g of the salt in 100 ml of 5% ammonium chloride solution.
75. Zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [297]	0.5M	Dissolve 150 g of the salt in 1 litre of water. Add 1-2 drops of conc. HNO_3 and mix uniformly.
76. Zinc sulfate $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ [287.38]	0.5M	Dissolve 144 g of the crystallised salt in 1 litre of water. Add 1-2 drops of conc. H_2SO_4 and mix uniformly.

Appendix-B8

Solutions of Salts of Some Rare Elements

Salt solutions	Approximate strength	Procedure
1. Ammonium metavanadate	0.1M	Dissolve 1.2 g of ammonium metavanadate, NH_4VO_3 , in 10 ml of 1 M sulfuric acid and dilute to 100 ml.
2. Ammonium molybdate*	0.25 M [Mo^{VI}]	Dissolve 44.2 g of ammonium hepta molybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, in a mixture of 60 ml of concentrated ammonia and 40 ml of water. Add 120g of ammonium nitrate. After complete dissolution, dilute the mixture to 1 litre with water. The solution must be acidified with conc. HNO_3 before using as a reagent.
	0.025 M	Dilute 1 ml of the 0.25 M solution described above to 10 ml.

Appendix-B8 (Continued)

Salt solutions	Approximate strength	Procedure
3. Cerium (III) nitrate	0.1 M	Dissolve 4.4 g of cerium (III) nitrate hexahydrate, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, in 10 ml of 2 M nitric acid and dilute to 100 ml with water.
4. Cerium (IV) sulfate	0.1M	Dissolve 4 g of cerium (IV) sulfate tetrahydrate, $\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ in a cold mixture of 50 ml of water and 5 ml of conc. sulfuric acid and dilute the solution to 100 ml with water.
5. Cerium (IV) diammonium sulfate dihydrate (ceric ammonium sulfate)	0.1M	Dissolve 6.4 g of cerium (IV) diammonium sulfate dihydrate, $\text{Ce}(\text{SO}_4)_2 \cdot 2(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$, in a cold mixture of 50 ml of water and 5 ml of concentrated sulfuric acid and dilute the solution to 100 ml with water.
6. Lanthanum nitrate	0.1M	Dissolve 4.33 g of lanthanum nitrate hexahydrate, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in 100 ml of water.
7. Lithium chloride	1M	Dissolve 4.2 g of anhydrous lithium chloride LiCl or 6 g of lithium chloride monohydrate $\text{LiCl} \cdot \text{H}_2\text{O}$ in water and dilute to 100 ml with water.
8. Osmium tetroxide (Osmic acid)	1%	Dissolve 1 g of osmium tetroxide (osmic acid), OsO_4 , in 10 ml of 1 M sulfuric acid and dilute the solution to 100 ml with water. Note: The solution is available commercially.
9. Palladium chloride	1%	Dissolve 1 g of palladium chloride, PdCl_2 , in water and dilute the solution to 100 ml.
10. Phosphomolybdic acid*	5%	Dissolve 0.5g of dodecamolybdophosphoric acid icositetrahydrate, $[\text{H}_3\text{PO}_4 \cdot 12\text{MoO}_3 \cdot 24\text{H}_2\text{O}]$ in 10 ml of water. Note: The solution does not keep well.
11. Sodium metavanadate	0.1M	Dissolve 1.2 g of sodium metavanadate, NaVO_3 , in 10 ml of 1 M sulfuric acid and dilute the solution to 100 ml with water.

Appendix-B8 (Continued)

Salt solutions	Approximate strength	Procedure
12. Sodium selenate [#]	0.1M	Dissolve 3.7 g of sodium selenate decahydrate, $\text{NaSeO}_4 \cdot 10\text{H}_2\text{O}$ in water and dilute to 100 ml.
13. Sodium selenite [#]	0.1M	Dissolve 1.73 g of sodium selenite, Na_2SeO_3 , in 100 ml of water.
14. Sodium tellurate [#]	0.1M	Dissolve 2.74 g of sodium tellurate dihydrate, $\text{Na}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$, in water and dilute to 100 ml.
15. Sodium tellurite [#]	0.1M	Dissolve 2.22 g of sodium tellurite Na_2TeO_3 in 100 ml of water.
16. Sodium tungstate	0.2M	Dissolve 6.6 g of sodium tungstate dihydrate, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, in water and dilute to 100 ml.
17. Thallium (III) chloride [#]	0.2M	Dissolve 4.57 g of thallium (III) oxide, Tl_2O_3 , in 5 ml of 6M hydrochloric acid, evaporate the solution to dryness (Fume Cupboard), dissolve the residue in water and dilute to 100 ml.
18. Thallium (I) nitrate [#]	0.05M	Dissolve 1.33 g of thallium (I) nitrate, TlNO_3 in 100 ml of water.
	Saturated	Shake 1 g of TlNO_3 with 10 ml of water, allow to stand. Use the clear supernatant liquid for the test.
19. Thorium nitrate	0.1M	Dissolve 5.88 g of thorium nitrate hexahydrate, $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$, in a mixture of 50 ml of water and 2.5 ml of concentrated nitric acid, dilute to 100 ml with water.
20. Titanium (IV) chloride	10%	Add 10 ml of liquid titanium tetrachloride, TiCl_4 , to 90 ml of 6M hydrochloric acid and mix uniformly.
21. Titanium (III) sulfate*	15%	Available commercially, but contains ~15% of Ti(IV) sulfate and also free sulfuric acid. Note: It is violet coloured. On standing, it is slowly oxidized to colourless Ti(IV) sulfate.

Appendix-B8 (Continued)

Salt solutions	Approximate strength	Procedure
22. Titanium (IV) sulfate	0.2M	(i) Dilute 33 ml of 15% (w/v) commercial titanium (IV) sulfate solution to 10 ml with 1 M sulfuric acid. (ii) Fuse ~1.6 g of TiO_2 with ~12-15g of potassium hydrogensulfate (KHSO_4) in a silica or a porcelain crucible. Cool and extract the fused mass with hot 3M sulfuric acid, filter and dilute to 100 ml with the same acid.
23. Zirconyl chloride	0.1 M	Dissolve 3.22 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 20 ml of conc. HCl and dilute the solution to 100 ml with water.
24. Zirconyl nitrate	0.1M	Dissolve 2.62 g of $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in 10 ml of 2M HNO_3 and dilute the solution to 100 ml with water.

Appendix-B9

Reagents Prepared in the Laboratory

Reagents	Approximate strength	Procedure
1. Bromine-water Br [79.904] Note: Use of hand gloves and eye protector are strongly recommended.	~1.3 M (saturated)	Add carefully [Caution Corrosive] ~3.5 ml of liquid bromine into ~100 ml of water taken in a stoppered conical flask, shake until almost complete dissolution. Add a few more drops of bromine to ensure slight excess.
2. Chlorine-water Cl [35.453] (cf. Fig. 3.10)	~0.18M (saturated)	Saturate 200 ml of water with chlorine gas, generated by dropping 6M HCl on to a slurry of calcium hypochlorite and gypsum or concentrated HCl upon KMnO_4 . Preserve the solution in well corked dark coloured bottle in a cool place away from light. The saturated solution contains ~6.5 g of chlorine per litre.

Appendix-B9 (Continued)

Reagents	Approximate strength	Procedure
3. Iodine (potassium triiodide) solution: Note: Don't use metallic or plastic spatula for transferring solid iodine. Use glass/porcelain made spoons.	0.1N	Dissolve 12.7 g of iodine crystals in a solution of 20 g of pure potassium iodide in ~100 ml of water and dilute to 1 litre with water.
4. SO ₂ -water (Sulfurous acid) (cf. Fig. 3.9)	~0.3N (saturated)	Pass into ~200 ml of ice cold water a stream of SO ₂ gas, generated by dropping dilute (~8M)H ₂ SO ₄ into a saturated solution of sodium sulfite in water until saturation. Preserve the solution in a well corked dark coloured bottle in a cool place. The saturated solution contains 6-7% of SO ₂ by weight.
5. H ₂ S - water (cf. Fig. 3.8)	~0.1 M (saturated)	Pass H ₂ S gas, generated from FeS and dilute H ₂ SO ₄ in Kipp's apparatus, through a bubbler and then into ~1 litre of water contained in a dark coloured bottle until saturation. Cork the bottle tightly with a rubber cork and preserve the solution in a cool and dark place. 1 g. H ₂ S dissolves in ~314 ml of water at 30°C and in 242 ml of water at 20°C at 1 atmosphere.
6. Starch solution		Make a thin paste of ~1 g of soluble starch with a little cold water and add the paste into 50 ml of boiling water with vigorous stirring. Continue boiling for 2-3 minutes until a clear solution results. Cool to room temperature. Preserve in a clean well stoppered bottle. ~1g of potassium iodide and 4-5 drops of chloroform may be added to improve the keeping quality of the solution.

Appendix-B10

Special Reagents

Reagent	Approximate strength	Procedure
1. Alizarin	Saturated	Shake 2g of alizarin ($C_{14}H_8O_4$) with 10 ml of 96% ethanol. Allow to stand, use the clear solution for the tests.
2. Alizarin-S or Alizarin red-S	2%	Dissolve 2 g of alizarin red-S (sodium alizarin sulfonate, $C_{14}H_7O_4 \cdot SO_3Na \cdot H_2O$) in 100 ml of water.
	0.1%	0.1 g/100 ml of water by the same procedure as above.
3. Aluminon reagent	0.1%	Dissolve 0.1g aluminon (triammonium aurin tricarboxylate ($C_{22}H_{23}N_3O_9$) in 100 ml of water.
4. Ammonium molybdate-quinine sulfate reagent*	4%/0.1%	Dissolve 4g of ammonium hepta molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) in 20 ml of water and add to this solution with stirring a solution of 0.1 g of quinine sulfate ($C_{20}H_{24}N_2O_2 \cdot H_2SO_4 \cdot 2H_2O$) in 80 ml concentrated nitric acid.
5. Ammonium tetrathio-cyanatomercurate (or ammonium mercurio-thiocyanate). (NH_4) ₂ [Hg(SCN) ₄]	0.3 M (in $HgCl_2$)	Dissolve 9 g of ammonium thiocyanate (NH_4SCN) and 8 g of mercuric chloride ($HgCl_2$) in water, dilute the mixture to 100 ml and mix uniformly.
6. Aniline sulfate*	1%	Dissolve 1g of aniline sulfate [$C_6H_5NH_2$] ₂ ·H ₂ SO ₄ in 100 ml of water. Preserve the solution in a dark coloured bottle.
7. Anthranilic acid*	5%	Dissolve 0.5g of anthranilic acid <i>o</i> -($H_2N \cdot C_6H_4 \cdot COOH$) in 10 ml of 96% ethanol.
8. Ascorbic acid S	0.05M	Dissolve ~1g of ascorbic acid ($C_6H_8O_6$) in 100 ml of water.
9. Benzidine	0.05%	Dissolve 0.05g of benzidine or its hydrochloride in 10 ml of concentrated acetic acid and dilute with water to 100 ml.

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
10. α -Benzoin oxime \$ (Cupron)	5%	Dissolve 5g of α -benzoin oxime [$C_6H_5CH(OH).C(NO_2H).C_6H_5$], in 96% ethanol and dilute to 100 ml with the same solvent.
11. 2,2'-Bipyridine* (highly expensive)	2%	Dissolve 0.02 g of the 2,2'-bipyridine in 1 ml of 0.1M hydrochloric acid or 1 ml of 96% ethanol.
12. Bis-(p-nitrophenyl) carbazine \$	0.1%	Dissolve 0.1 g of bis-(p-nitrophenyl) carbazine (ie., p, p'-dinitro-1, 5-diphenyl carbazine) $OC(NHNH.C_6H_4-NO_2)_2$ in 100 ml of 96% ethanol.
13. Cacotheline	0.25%	Dissolve 0.25 g of cacotheline (nitrobruciquinone hydrate, $C_{21}H_{21}O_7N_3$) in 100 ml of water.
14. Catechol (Pyrocatechol)*	10%	Dissolve 10 g of catechol (i.e. 1, 2-dihydroxybenzene), $o-C_6H_4(OH)_2$, in 100 ml of water.
15. Chloramine-T \$	0.05M	Dissolve 1.4 g of chloramine-T ($H_3C-C_6H_4-SO_2N-Na^+Cl^- \cdot 3H_2O$) in water and dilute to 100 ml.
16. Chromotropic acid \$	...	Shake 0.1g of chromotropic acid, sodium salt, (1,8-dihydroxynaphthalene-3,6-disulfonic acid, sodium salt), $C_{10}H_6O_8S_2Na_2$ with 5 ml of water and allow to stand. Use the clear supernatant liquid for the tests.
17. Cinconine-potassium iodide	1%	Dissolve 1 g of cinconine in a mixture of 99 ml of water and 1 ml of 2 M nitric acid. Cool the mixture and dissolve 1 g of potassium iodide in this solution. Mix uniformly. The reagent is stable for two weeks.
18. Cupferron \$	2%	Dissolve 2 g of cupferron [$C_6H_5N(NO)O-NH_4^+$] in 100 ml of water, add 1 g of ammonium carbonate to enhance stability.

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
19. Curcumin*	Saturated	Shake 0.5 g of curcumin $[H_3CC_6H_3(OH).CH:CH.CO)_2CH_2]$ with 10 ml of 96% ethanol. Allow to stand. Use the clear supernatant liquid for the tests.
20. Diammineargentato nitrate : $[Ag(NH_3)_2]NO_3^*$ Note: Discard the unused reagent after test, because silver azide AgN_3 that precipitates on standing, may cause <i>serious explosion</i> .	0.1M	Add 2 M aqueous ammonia solution to 10 ml of 0.1M silver nitrate solution until the precipitate first formed is just redissolved.
21. Diazine green (Janus green)	0.1%	Dissolve 0.01g of diazine green (colour index 11050) in 100 ml of water.
22. Di-(4-dimethylaminodiphenyl) methane (tetrabase)	1%	Dissolve 0.1g of tetrabase, $[(H_3C)_2N.C_6H_4]_2CH_2$, in 10 ml of chloroform.
23. 4-Dimethylaminobenzene-azo-phenyl-arsonic acid §	0.1%	Dissolve 0.1g of 4'-dimethylamino azobenzene-4-phenylarsonic acid, $(H_3C)_2N.C_6H_4.N:N.C_6H_4.AsO(OH)_2$ in 5 ml of concentrated hydrochloric acid and then dilute to 100 ml with 96% ethanol.
24. 4-Dimethylaminobenzylidene-rhodanine §	0.3%	Dissolve 30 mg of commercial 4-dimethylaminobenzylidene-rhodanine reagent in 10 ml of acetone.
25. Dimethylglyoxime	1%	Dissolve 1g of dimethylglyoxime, $[H_3C.C(NO_2).C(NO_2).CH_3]$, in 100 ml of 96% ethanol.
26. N N-Dimethyl- <i>p</i> -phenylene-diamine dihydrochloride*	1%	Dissolve 1g of N, N-dimethyl- <i>p</i> -phenylenediamine dihydrochloride, $H_2N.C_6H_4.N(CH_3)_2.2HCl$ in water and dilute to 100 ml. [the sulfate salt $H_2N.C_6H_4.N(CH_3)_2.H_2SO_4$ may also be used.]
27. Diphenylamine*	0.5%	Dissolve 0.5g of diphenylamine $(C_6H_5)_2NH$, in 85 ml of concentrated sulfuric acid and pour the solution slowly into 15 ml of ice cold water with stirring.

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
28. 1,5-Diphenylcarbazine \$	1% (in ethanol)	Dissolve 0.1g of 1,5-diphenylcarbazine (C_6H_5NHNH) ₂ CO in 10 ml of 96% ethanol. Note: The solution decomposes rapidly on exposure to air.
	0.2% (in acetic acid)	Dissolve 2 g of 1,5-diphenylcarbazine in 10 ml of glacial acetic acid and dilute the mixture to 100 ml with 96% ethanol.
29. Diphenylthiocarbazone (Dithizone)*	0.005%	Dissolve 5 mg of dithizone (diphenylthiocarbazone) [$C_6H_5N:N.C(=S).NHNH.C_6H_5$], in 100 ml of chloroform.
30. <i>p</i> -Dipicrylamine \$	1%	Mix 0.2 g of <i>p</i> -dipicrylamine (hexanitro diphenylamine), [$C_6H_2(NO_2)_3$] ₂ NH, 4 ml of 0.5 M sodium acetate and 16 ml of water. Boil the mixture for 2-3 minutes, allow to cool, filter and use the clear filtrate for the tests.
31. Dithiooxamide (Rubeanic acid)\$	0.5%	Dissolve 0.5 g of rubeanic acid [$H_2N.C(=S).C(=S).NH_2$], in 100 ml of 96% ethanol.
	0.02% (in acetic acid)	Dissolve 20 mg of rubeanic acid in 100 ml of glacial acetic acid. Note: The solution decomposes rapidly. It should be prepared just before use each time.
32. Ferron	0.2%	Dissolve 0.2g of ferron (8-hydroxy-7-iodo-quinoline-5-sulfonic acid). [$C_9H_6O_4NSI$], in 100 ml of water.
33. Fluorescein reagent	1%	Shake 1g of fluorescein (colour index 45350) with 50 ml of 96% ethanol and 50 ml of water. Allow to stand for 24 hours, filter and use the filtrate for the tests.
34. Ferrioin	0.025M	Dissolve 1.624 g of 1, 10-phenanthroline hydrochloride and 0.695 g of

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
35. Formaldehyde (4%)- Sodium carbonate (0.05M) reagent S		$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 100 ml of water. Alternatively, dissolve 1.485 g of 1, 10-phenanthroline monohydrate (F.W. 198) and 0.98 g of Mohr's salt (F.W. 392) in 7.5 ml of 1 M hydrochloric acid and dilute to 100 ml with water. Mix 10 ml of 40% formaline, 10 ml of 0.5M sodium carbonate and 50 ml of water, dilute the mixture to 100 ml with water. Note: The reagent decomposes on standing.
36. Fuchsin	0.1%	Dissolve 0.1g of fuchsin (magenta, colour Index 42500) in 100 ml of water.
	0.015%	Dissolve 15 mg of fuchsin in 100 ml of water.
37. Gallocyanine	1%	Dissolve 1g of gallocyanine [$\text{C}_{15}\text{H}_{12}\text{O}_5\text{N}_2$] in 100 ml water.
38. Gold (III) chloride (Expensive)	0.33 M (in Au)	Dissolve 1.3 g of sodium tetrachloroaurate (III) dihydrate, $\text{Na}[\text{AuCl}_4] \cdot 2\text{H}_2\text{O}$, in 10 ml of water. Alternatively, dissolve ~0.65 g of gold in 5 ml of aqua-regia, evaporate the solution to dryness (Fume Chamber) and dissolve the residue in 10 ml of water.
39. Hexachloroplatinic acid (IV) (Expensive)	0.5M	Dissolve 0.26 g of hexachloroplatinic acid (IV), $\text{H}_2[\text{PtCl}_6] \cdot 6\text{H}_2\text{O}$ in 10 ml of water.
40. Hydrazine sulfate*	Saturated	Shake 2g of hydrazine sulfate [$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$] with 5 ml of water vigorously. Use the supernatant liquid for the tests.
41. Hydrogen peroxide* [To be handled with	30% (100-volume)	Commercial concentrated hydrogen peroxide [H_2O_2] may contain small

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
great caution and stored in a refrigerator)	6% (20-volume)	amount of sulfuric acid or organic materials as stabilizer. Store in a dark coloured bottle in a cool place. Dilute 20 ml of '100-volume' H_2O_2 to 100 ml with water. Store in a dark coloured bottle in a cool place.
	3% (10-volume)	Dilute 10 ml of '100-volume' H_2O_2 to 100 ml with water. Store in dark coloured bottle in a cool place.
42. Hydroxylamine hydrochloride*	10%	Dissolve 10g of hydroxylamine hydrochloride $[NH_2OH.HCl]$ in 100 ml of water.
43. 8-Hydroxyquinoline (Oxine)	5% (in 0.1 M H_2SO_4)	Dissolve 5g of 8-hydroxyquinoline (oxine) $[C_9H_7ON]$ in a mixture of 90 ml of water and 10 ml of 1M sulfuric acid. The reagent is stable for months.
	2% (in acetic acid)	Dissolve 2 g of oxine in 100 ml of 2M acetic acid.
	1% (in ethanol)	Dissolve 1 g of oxine in 100 ml of 96% ethanol.
44. Indigo solution	1%	Dissolve 0.1g of indigo $[C_{16}H_{10}O_2N_2]$, colour index 73000) in 10 ml of concentrated sulfuric acid.
45. Indole	0.015%	Dissolve 15mg of indole $[C_6H_4NHCH.CH]$ in 100 ml of 96% ethanol.
46. Manganese nitrate (or sulfate)- Silver nitrate reagent*	0.1M (Mn^{2+}) 0.2 M (Ag^+)	Dissolve 2.87g of manganese nitrate hexahydrate $[Mn(NO_3)_2.6H_2O]$, in 40 ml of water (solution-A). Dissolve 3.55 g of silver nitrate $[AgNO_3]$, in 40 ml of water (solution-B). Mix solution-A with solution-B and add drops of 2M sodium hydroxide solution until a black precipitate starts to form. Filter and dilute the filtrate to 100 ml with water, keep in a dark coloured bottle.

Reagent	Approximate strength	Procedure
47. Manganese nitrate-Silver nitrate-potassium fluoride reagent*	...	To 100 ml of manganese nitrate-silver nitrate reagent described above add 3.5 g of potassium fluoride dissolved in 50 ml of water. Boil, cool to room temperature and filter off the dark coloured precipitate. Use the clear filtrate for the tests.
48. α -Naphthylamine* (for the Griess-Ilosvay test)	0.3%	Boil 0.3 g of α -naphthylamine [$C_{10}H_7NH_2$] with 70 ml of water for a few minutes. Decant the clear liquid, cool and add 30 ml of glacial acetic acid. If the solution is intensely coloured, add a small amount of zinc dust, stir vigorously with a glass rod and filter. Use the clear filtrate for the tests.
49. Nessler's reagent*	0.1M ($K_2[HgI_4]$) 4M(KOH)	Dissolve 5.5 g of mercuric chloride [$HgCl_2$] in 100 ml of water (soln. A). Dissolve 3.5g of potassium iodide [KI] in 10 ml of water (soln. B). Dissolve 45 g of potassium hydroxide [KOH], in 80 ml of water (soln. C). Now add dropwise with stirring soln. A to soln. B until a faint but permanent turbidity appears, then add soln. C with stirring, mix uniformly. Dilute to 200 ml with water, allow to stand over night, decant or syphon off the clear supernatant liquid, for use in the tests.
50. Nickel ethylenediamine nitrate reagent*		Add drops of ethylenediamine ($H_2NCH_2CH_2NH_2$, en) to 2 ml of 0.5M nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] solution, until a violet colour appears, due to the formation of the complex $[Ni(en)_3]^{2+}$ ion.
51. Nitrazene yellow	0.1%	Dissolve 0.1 g of nitrazene yellow (2, 4-dinitrobenzeneazo)-1-naphthol-4, 8-disulfonic acid disodium salt (Colour Index 14890) in 100 ml of water.

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
52. 2-Nitrobenzaldehyde*	0.5%	Dissolve 5 mg of 2-nitrobenzaldehyde [$\text{O}_2\text{N.C}_6\text{H}_4\text{-CHO}$], in 1 ml of 2M sodium hydroxide solution.
53. 4-Nitrobenzene-azo-1-naphthol (Magneson-II)*	0.5%	Dissolve 0.5 g of 4-(4-nitrophenylazo)-1-naphthol (magneson-II) [$\text{O}_2\text{N.C}_6\text{H}_4\text{.N:N.C}_{10}\text{H}_6\text{.OH}$], in of 20 ml of 1M sodium hydroxide solution. Dilute the solution to 100 ml with water.
54. 4-Nitrobenzene-azo-chromotropic acid*	0.005%	Dissolve 5 mg of 4-(4-nitrophenylazo) chromotropic acid, sodium salt, (Chromotrope-2B, Colour Index 16575) in 100 ml of concentrated sulfuric acid.
55. 4-Nitrobenzenediazonium chloride reagent \$		Dissolve 1g of 4-nitroaniline [$\text{O}_2\text{N.C}_6\text{H}_4\text{-NH}_2$] in 25 ml of 2M hydrochloric acid and dilute the solution to 160 ml with water. Cool in an ice-water both and add 20 ml of 5% sodium nitrite (NaNO_2) solution, stirr until the precipitate dissolves and a clear solution results. The reagent on keeping, gradually becomes turbid, but can be used again after filtering off the precipitate.
56. 3-Nitrobenzoic acid*	Saturated	Dissolve 1g of 3-nitrobenzoic acid [$\text{O}_2\text{N.C}_6\text{H}_4\text{.COOH}$] in 250 ml of water by warming the mixture on a hot water bath. Allow to cool to room temperature and filter. Use the filtrate for the tests.
57. Nitron reagent*	5%	Dissolve 5 g of nitron [$\text{C}_{20}\text{H}_{16}\text{N}_4$] in 100 ml of 2M acetic acid.
58. 4-(4-Nitrophenylazo) resorcinol* [Magneson-I]	0.5%	Dissolve 0.5g of 4-(4-nitrophenylazo) resorcinol, (magneson-I), [$\text{O}_2\text{N.C}_6\text{H}_4\text{.N:N.C}_6\text{H}_2(\text{OH})_2\text{CH}_3$], in 20 ml of 1 M sodium hydroxide.
59. 4-Nitronaphthalene-diazoamino-azobenzene, [Cadion 2B]\$	0.02%	Dissolve 0.02 g of Cadion 2B [$\text{O}_2\text{N.C}_{10}\text{H}_6\text{.N:N.NH.C}_6\text{H}_4\text{.N:N.C}_6\text{H}_5$] in 100 ml of 96% ethanol containing 1 ml of 2M potassium hydroxide.

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
60. 1-Nitroso-2-naphthol (α -Nitroso- β -naphthol)	1%	Dissolve 1g of 1-nitroso-2-naphthol $[C_{10}H_6(OH)NO]$, in 100 ml of 9M acetic acid. Note: Instead of acetic acid, 100 ml of 96% ethanol or acetone may also be used.
61. 1,10-Phenanthroline	0.1%	Dissolve 0.1 g of 1,10-phenanthroline hydrate $[C_{12}H_8N_2 \cdot H_2O]$ in 100 ml of water.
62. <i>p</i> -Phenetidine hydrochloride*	2%	Dissolve 2g of <i>p</i> -phenetidine, $[C_2H_5 \cdot O \cdot C_6H_4 \cdot NH_2]$, in 5 ml of concentrated hydrochloric acid and dilute the solution to 100 ml with water. Note: Complete dissolution may occur after dilution.
63. <i>p</i> -Phenetidine*	0.1%	Dissolve 0.1g of <i>p</i> -phenetidine $[C_2H_5 \cdot O \cdot C_6H_4 \cdot NH_2]$ in 100 ml of 2M hydrochloric acid.
64. Phenylarsonic acid \$		Shake 1g of phenylarsonic acid $[C_6H_5As(=O)(OH)_2]$ with 10 ml of water. Use the clear liquid for the tests.
65. Phenylhydrazine*		Dissolve 1g of phenylhydrazine $[C_6H_5NHNH_2]$, in 2 ml of glacial acetic acid.
66. Picrolonic acid (Picrolonic acid)	Saturated	Shake 1g of picrolonic acid, $C_{10}H_8O_5N_4$ with 5 ml of water. Allow to stand, use the clear supernatant liquid for the tests.
67. Propylarsonic acid \$	5%	Dissolve 0.5g of propylarsonic acid $[CH_3CH_2CH_2As(=O)(OH)_2]$, in 10 ml of water.
68. Pyrogallol*	10%	Dissolve 0.5g of pyrogallol, $[C_6H_3(OH)_3]$, in 5 ml of water. The reagent slowly decomposes.
69. Pyrrole*	1%	Dissolve 1g of pyrrole $[C_4H_5N]$, in 100 ml of (addehyde-free) 96% ethanol.

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
70. Quinaldinic acid* (Na-Salt)	1%	Dissolve 1g of quinaldinic acid, $[C_{10}H_7O_2N]$ in 5 ml of 2M sodium hydroxide solution and dilute to 100 ml with water.
71. Quinalizarin*	0.05% (in NaOH)	Dissolve 0.05g of quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) in a mixture of 50 ml of water and 5 ml of 2M sodium hydroxide. Dilute the solution to 100 ml with water.
	0.05% (in pyridine)	Dissolve 0.01g of quinalizarin in 2 ml of pyridine and dilute the solution to 20 ml with acetone.
72. Rhodamine-B	0.01%	Dissolve 0.01g of Rhodamine-B, $[C_{28}H_{31}N_2O_3]$, Colour Index 45170), in 100 ml of water.
	0.05%	Dissolve 0.05 g of Rhodamine-B in 100 ml of 2M hydrochloric acid containing 15g of potassium chloride dissolved in it.
73. Salicylaldehyde oxime (Salicylaldoxime)*	1%	Dissolve 1g of salicylaldoxime, $[(HO)-C_6H_4-CH(=NOH)]$, in 5 ml of cold 96% ethanol and pour the solution dropwise into 95ml of water at a temperature not exceeding 80°C. Shake the mixture vigorously, filter if necessary. Use the clear filtrate for the tests.
74. Sebacic acid	Saturated	Shake 5g of sebacic acid $[C_4H_8COOH]_2$, with 95 ml of water, allow to stand for 24 hours. Use the clear supernatant liquid for the tests.
75. Sodium azide-iodine reagent*		Dissolve 3g of sodium azide $[NaN_3]$ in 100 ml of 0.05M iodine (NaI_3 or KI_3) solution.
76. Sodium carbonate- Phenolphthalin reagent*	...	Mix 1 ml of 0.005M sodium carbonate with 2 ml of 0.5% phenolphthalin and dilute the mixture to 10 ml with water.

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
77. Sodium 1-nitroso-2-hydroxynaphthalene-3, 6-disulfonate. [Nitroso-R-salt]*	1%	Dissolve 1g of sodium 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate [Nitroso R-salt, $C_{10}H_4(OH)(SO_3Na)_2NO$] in 100 ml of water.
78. Sodium rhodizonate \$	0.5%	Dissolve 0.05 g of sodium rhodizonate [rhodizonic acid, disodium salt, $C_6O_6Na_2$], in 10 ml of water. Note: The solution decomposes rapidly.
79. Di-sodium tetrahydroxostannate (II) reagent (Sodium stannite)*	0.125%	Add drops of 2M sodium hydroxide solution to 2 ml of 0.25M tin(II) chloride with vigorous shaking, until the precipitate initially formed just dissolves (about ~2 ml of 2M NaOH solution may be required in excess). Note: The reagent should be prepared just before use, as it is oxidized rapidly.
80. Sodium tetraphenyl boron \$	0.1M	Dissolve 3.42g of sodium tetraphenyl boron, $[NaB(C_6H_5)_4]$, in 100 ml of water. Note: The solution does not keep for a long time.
81. Sulfanilic acid	1%	Dissolve 1g of sulfanilic acid [4-amino-benzene sulfonic acid, $H_2N-C_6H_4-SO_3H$], in 100 ml of 30% warm acetic acid and allow the solution to cool.
82. Tannic acid	5%	Shake 5g of tannic acid, $C_{76}H_{52}O_{46}$, with 100 ml of water, allow to stand and filter. Use the clear filtrate for the tests.
83. Tartaric acid-ammonium molybdate reagent \$	15%/ 0.25M	Dissolve 15g of tartaric acid in 100 ml of 0.25 M ammonium molybdate reagent.
84. Thiourea*	5% (in 5M HCl)	Dissolve 5 g. of thiourea, $S=C(NH_2)_2$, in a mixture of 43 ml of concentrated hydrochloric acid and 50 ml of water, dilute to 100 ml.

Appendix-B10 (Continued)

Reagent	Approximate strength	Procedure
85. Titan yellow (Clayton yellow)	0.1%	Dissolve 0.1g of Titan yellow (Colour index 19540) in 100 ml of water.
86. Uranyl acetate	0.1M	Dissolve 4.24g of uranyl acetate, $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in a mixture of 20 ml of water and 3 ml of glacial acetic acid. After complete dissolution, dilute the solution to 100 ml with water.
87. Uranylmagnesium acetate reagent*	0.12M [UO_2^{2+}] 0.77M [Mg^{2+}]	Dissolve 10g of uranyl acetate dihydrate, $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in a mixture of 6 ml of glacial acetic acid and 100 ml of water (<i>solution-A</i>). Dissolve 33g of magnesium acetate tetrahydrate, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, in a mixture of 100 ml of glacial acetic acid and 100 ml of water (<i>solution-B</i>). Mix <i>solution-A</i> with <i>solution-B</i> , stirr to mix uniformly, allow to stand for 24 hours. Filter and use the clear filtrate for the tests.
88. Uranyl nitrate	0.1M	Dissolve 5.02g of uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in water and dilute to 100 ml.
89. Uranylzinc acetate reagent*	0.25 M [UO_2^{2+}] 1.37M [Zn^{2+}]	Dissolve 10g of uranyl acetate dihydrate, $\text{UO}_2(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ in a mixture of 5 ml of glacial acetic acid and 20 ml of water and dilute to 50 ml (<i>solution-A</i>). Dissolve 30 g of zinc acetate dihydrate, $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, in a mixture of 5 ml of glacial acetic acid and 20 ml of water and dilute to 50 ml with water (<i>solution-B</i>). Mix <i>solution-A</i> with <i>solution-B</i> . Add 0.5 g of sodium chloride (NaCl), stirr to mix uniformly, allow to stand for 24 hours. Filter and use the filtrate for the tests.
90. Zinc hexaammine hydroxide		Add 12.5 ml of 2M potassium hydroxide to 25 ml of 0.5 M zinc nitrate. Filter and wash the precipitate with water and dissolve the precipitate on the filter paper with 1:1 aqueous NH_3 solution, pouring the solution repeatedly on the filter, until complete dissolution.



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Abbreviations: *c* = Confirmation, *d* = Detection, *i* = Identification, *p* = Preparation, *r* = Reactions, *sp* = Separation, *sc* = Scheme, *t* = Table.

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